psa

PHOTOGRAPHIC SCIENCE and TECHNIQUE

FOR MAY 1954

Series II, Volume 1, Number 2

TABLE OF CONTENTS

Document Reproduction by Photography in the United States	Walter Clark	31
Making American Standards Effective	Carolyn Locher	37
Report to the PSA Standards Committee on the Activities of the ASA Committee on Photographic Sensitometry (PH2)	H. R. Sprentall	40
Better Exposure Guide Numbers	Ralph E. Farnham	40
The Activity of Photographic Researches in Japan	Shinnosuke Fukushima	42
Mechanisms of Color-Sensitization	Lester Horwitz	43
Silver Bromide Photo Cells	John Eggert and Hans Amsler	52
Some New Optical Systems for Special Photographic Applications	H. Joe Meyer	56
An Inorganic Developer Reactivated by Electrolysis	A. A. Rasch and J. I. Crabtree	59
Microradiography and Autoradiography Symposium	Anon	68

TECHNICAL QUARTERLY
OFFICIAL PUBLICATION
OF THE PHOTOGRAPHIC
SOCIETY OF AMERICA

NOTES OF TECHNICAL INTEREST

Easy Identification of Safety Film*

In order to distinguish safety film from the ordinary flammable film, indices are mostly printed on the border of the film. These indices are repeated at short intervals. To be sure, however, whether in this case a film-roll completely consists of safety film, the whole roll must be unwound and verified over its entire length.

Using fluorescing substances is a better solution of the problem: the safety film is rendered fluorescing in such a way that when lighted with ultraviolet light, without unwinding the roll, it is immediately determined whether the roll is not, or wholly, or only partly composed of safety film.

Products, which may be used for the purpose, mostly belong to the organic series and possess a rather complicated structure. Good results may be attained a.o. with: anthracene *or* phenanthrene nitrile *or* N-N′-bis (2-amino-4-mono-ethanolamino-1-3-5 triazinyl-6)-4-4′-diamino stilbene-2-2′-disulphonic acid (sodium salt) *or* ethyl-dihydrocollidine-dicarboxylate *or* 4-5 diphenyl imidazolone-2 *or* 4-5-difurane imidazolone-2.

Quantitative Organic Analysis

The second edition of "Quantitative Organic Analysis Via Functional Groups" by Sidney Siggia has been published by John Wiley & Sons, 440 Fourth Avenue, New York 16.

The new, extensively revised edition retains the original format which made it particularly useful as a fingertip reference in the industrial laboratory. New procedures have been added, however, and older ones, replaced since 1949 by more effective techniques, have been deleted. Dr. Siggia has added a section on the use of quantitative analysis in the identification of organic compounds, including the use of phase diagrams in organic analysis of mixtures.

Known for its exclusive attention to functional group analysis, the book gives complete information for each procedure, including sample sizes and reagents. Each procedure is discussed from every point of view—the chemistry involved, various interferences to analysis, range of applicability, and accuracy and precision of the results.

Dr. Siggia, who is a research analyst in the Central Research Laboratory of the General Aniline and Film Corporation, has used satisfactorily all the methods he describes. His superior selection was made on the basis of simplicity, accuracy, precision, and the general applicability of a given method. Only standard analytical equipment is required in most procedures, and where special equipment is needed, it is easy to construct or relatively inexpensive to purchase.

The second edition of "Quantitative Organic Analysis Via Functional Groups" contains 227 pages and is priced at $5.00.

International Symposium on High-Speed Photography and Cinematography

The 2nd International Symposium on High-Speed Photography and Cinematography will take place in Paris from 22 to 28 September 1954. The 1st Symposium was held in Washington, D.C. in October 1952, under the sponsorship of the Society of Motion Picture and Television Engineers.

The Symposium is being arranged by the French Society of Motion Picture Engineers and Technicians (Association Française des Ingénieurs et Techniciens du Cin'ma) with the cooperation of the Deutsche Kinotechnische Gesellschaft, the Samsfundet Svenska Film Ingenjörer and possibly two or three other European societies.

Communications concerning the Symposium and applications to attend should be sent to the Secretary of the Organizing Committee, Mr. P. Naslin, Laboratoire Central de l'Armement, Fort de Montrouge, ARCUEIL (Seine), Paris.

Papers will be read, not only on optical, mechanical, electrical, and electronic methods, techniques, instruments, and accessories in the use of high-speed photography, radiography, cinematography and radiocinematography, but also on the applications of these techniques to the study of rapid events in the various scientific and technical fields (physics, aerodynamics, mechanical engineering, machine-tools, metallurgy, electrical engineering, power-engineering, ballistics, medicine, surgery, biology, etc.).

* Reprinted from Photorama No. 12, 1953 by permission of the editor, H. Craeybeckx.

Series II, Vol. 1, No. 2 ☆ PHOTOGRAPHIC SCIENCE AND TECHNIQUE ☆ MAY 1954

Official publication of the Photographic Society of America published quarterly at 20th and Northampton Streets, Easton, Pennsylvania. Copyright 1954 by the Photographic Society of America. Application for entry as second-class matter at the Post Office, Easton, Pa. is pending.

Paul Arnold, APSA, Hon. PSA, EDITOR
26 Hotchkiss Street, South
Binghamton, New York

H. Lou Gibson, FPSA, Asst. EDITOR
343 State Street
Rochester 4, New York

BOARD OF ASSOCIATE EDITORS

Morris Gurtie, APSA	5412 N. Bernard Street	Chicago 25, Illinois
R. C. Hakanson	10322 Lake Shore Boulevard	Cleveland 8, Ohio
Hutson Howell	700 Commonwealth Avenue	Boston, Massachusetts
T. Howard James, APSA	Kodak Research Laboratories	Rochester 4, New York
Peter Krause, APSA	69 Bourndale Road, South	Manhasset, New York
A. E. Neumer	635 St. Paul Street	Rochester 2, New York
Elmer S. Phillips	Roberts Hall, Cornell University	Ithaca, New York
John B. Taylor	118 Laurel Avenue	Binghamton, New York

PHOTOGRAPHIC SCIENCE AND TECHNIQUE is dedicated to the publication of scientific and technical papers dealing with the theory and practice of photography. Its aim is to encourage the publication of authoritative articles describing original research, techniques, and the engineering aspects of new equipment in all fields of photography. It is intended to interest and inform the advanced amateurs, the professionals, the technologists, and the scientists who study or apply photographic processes.

Established in 1950, Photographic Science and Technique is prepared under the editorial management and control of the Technical Division of the Society. The first four volumes were issued as Section B of the PSA Journal and numbered 16B to 19B inclusively. As a separate publication, Series II, Volume 1, Number 1 started in the first quarter of 1954.

Members of the Photographic Society are entitled to receive both the monthly PSA Journal and this quarterly technical publication. Non-member subscriptions are available only to libraries, schools, and Government units at $5.00 a year ($9.00 for two years) for both publications together. Separate subscriptions are not available. Single copies, including back issues when available, $1.00 a copy. No extra charge for overseas mailing.

Address manuscripts and communications to the Editor. The Associate Editors are available for advice and assistance in the preparation of manuscripts. Unacceptable manuscripts will be returned if requested. Authors will be sent galley proofs for correction. Reprints may be ordered by the authors prior to publication.

The contents may not be reproduced without the written permission of the editor. No responsibility is assumed for the accuracy of statements by contributors but care will be taken to avoid the publication of errors. The publishing of opinions and conclusions expressed by authors does not necessarily indicate concurrence or endorsement by the editors, by the Technical Division, or by the Photographic Society of America.

DOCUMENT REPRODUCTION BY PHOTOGRAPHY IN THE UNITED STATES

Walter Clark, FPSA*

ABSTRACT

The great increase in the use of photography for the reproduction of documents in recent years results from the realization of its importance for effectively increasing the life of perishable documents, reducing the storage space of documents, and disseminating the information in documents as rapidly, as effectively, or as cheaply as possible. Many methods are widely employed. In the United States, there are certain aspects on which special emphasis has recently been laid. They include the intermediate film method for making paper copies, new direct positive papers, microcopying, extra-rapid processing, special image transfer techniques, and pseudo-photographic methods (electrostatic and "dry processing"). The quality of the micro-image and the problem of visual fatigue in using film readers have been specially studied.

THE GREAT INCREASE in the use of photography for the reproduction of documents in recent years results from the realization of its importance for disseminating the information in them as rapidly, as effectively, or as cheaply as possible, reducing the storage space of documents, and effectively increasing the life of perishable documents.

This discussion may, in a sense, be considered to be an extension of the two reports which were published in 1951 on photographic reproduction methods, one by UNESCO (United Nations Educational Scientific and Cultural Organization) and the other by OEEC (Organization for European Economic Co-operation).[1] The earliest emphasis was on direct copying onto paper and on microreproduction on rolls of film.[2,3] Both of these systems are now in wide use throughout the world and, in spite of many criticisms of the microfilm system, it is still a very widely used system of reproduction of documents.

Much of the literature and the deliberations of many committees have concerned themselves with the availability, storage, and dissemination of scientific and other learned material. They tend to overlook the importance of photographic reproduction in the commercial and industrial fields, with which most of the recent developments in the United States have been concerned.

The Intermediate Microfilm Method

There have been two developments from microfilm which have gained a lot of impetus recently. During the war, there was developed a system, known as Air-Graph in England and V-Mail in the United States, for handling correspondence with the armed forces in various parts of the world. In that system, letters written on special forms were photographed on 16mm film, which was processed and sent to various distribution centers where the film negatives were enlarged onto rolls of photographic paper, which was cut up and the resulting letters distributed to the addressees.

A number of organizations now use the intermediate microfilm method for producing photographic copies of documents on paper. When the volume is large, automatic and continuously operating systems are used. The United States Library of Congress Photoduplicating Service, which is one of the world's greatest producers of photographic copies of documents, uses automatic continuous systems based on 35mm and 16mm intermediate films.[4] In the Kodak Research Laboratories in Rochester, New York, which represents a moderate user of the system—the output of prints averaging about 5,000 copies per week at present—35mm microfilm negatives are used, and step enlargers in conjunction with stepwise paper advancers expose the enlarged copies on rolls of thin paper which are processed in continuous machines. In exposing the negatives, code marks are included to control the movement of the negatives and paper and operate the shutter in accordance with the number of copies of each document required. In general, it has been found that better definition results if the enlargements are made with the film and paper stationary during exposure rather than in enlargers in which film and paper move continuously.

Sheet microfilms are not used to any appreciable extent in the United States except as intermediates for making opaque positive cards to which reference is made below.

Another recent development in the use of microfilm is the Filmsort system.[5] One of the criticisms of microfilm in rolls is that the information on a roll is fixed in position and in relation to other information. Additional data cannot be added simply, shuffling is practically impossible, and cross reference is cumbersome. The Filmsort system attempts to improve this by incorporating separate frames or strips of microfilm in apertures in cards of conventional shape which can be filed and sorted in the normal manner. (Figure 1.) They can be read in special readers or enlarged to make paper reproductions. The films are inserted in all major types of filing cards including the electrical accounting cards such as those of the I.B.M., punched cards such as the Keysort, E-Z Sort, and other varieties, and in ordinary plain index cards. Strips of 16mm and 35mm film can also be assembled in sheaths to form an assembled sheet which can be filed and sorted. Information not recorded from the document can be combined with the film on the card to provide the index and the record. The Filmsort system, worked out in the U. S. Office of Strategic Services during the war, is now used in a variety of fields including

* Research Laboratories, Eastman Kodak Company, Rochester 4, New York. Presidential address to Section E, Royal Photographic Society Centenary, International Conference on the Science and Applications of Photography. London, September, 1953. To be published in the Proceedings of the Conference.

engineering drawings, credit reports, copies of insurance policies, case histories in hospitals, and legal documents. One interesting application is by the U. S. Department of Agriculture, which uses the method for filing copies of meat labels instead of filing the original labels in the form of cellophane wraps, cardboard cartons, meat casings, ham wrappers, and so on.

The Statfile system for reduced copying of engineering drawings onto sheet film is not used as such in the United States, although the problem of reduced-size storage of engineering drawings is ever present. So far, no decision has been made concerning the intermediate reduced-size transparency, what its size and form should be, whether it should be positive or negative, and what reduction can be tolerated in the enlarged paper reproduction as compared with the size of the original drawing. There is, however, a great interest in storing drawings in reduced size on film and at short notice being able to produce legible multiple copies on paper.

The Rapid Selector

Much thought has been given to designing machines which use microfilm carrying text matter and a code, so that information can be stored, found, and reproduced rapidly. The most talked-about machine of this type is probably the rapid selector proposed by Vannevar Bush, a variation of which is being developed by R. R. Shaw at the U. S. Department of Agriculture.[6] In the Shaw rapid selector, the code dots are such that six subjects can be recorded next to one page of text. The inquirer places in a machine a punched card, the arrangement of the punched holes in which is determined by the subject. Film is run through the machine and is projected optically onto the card. When the holes in the card correspond exactly with the dots on the film, a photoelectric system is triggered to fire a stroboscopic flash lamp, which makes a photographic enlargement of the appropriate text. There are, of course, many special problems, for instance, reproduction of frames of film which are close together, and moving the receiving medium intermittently and rapidly enough to avoid overlapping exposures.

Thought is being given to developing selectors built on the lines of the electronic computers. The development of optical-electrical-mechanical devices for use in bibliographic work is, however, still in its infancy, although the Shaw rapid selector has taught a lot.

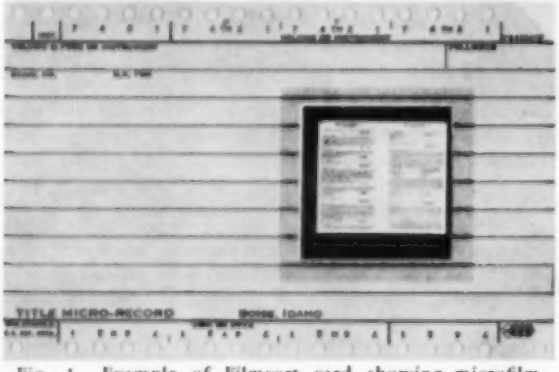

Fig. 1. Example of Filmsort card showing microfilm transparency inserted in window in card.

Document Copies on Paper

There has recently been a great increase in the use of microphotographs of documents on white cards to be read in magnifying reflecting projectors.[7,8,9] These should probably be known as micro-texts or micro-opaques or some such term in order to avoid trade marks such as "Microcard," "Microprint," "Microlex," and "Microstrip." A typical card is 3 by 5 inches in size, may carry reproductions of about 60 pages, and have extra bibliographic data on the front or back.

These cards are usually of special photographic paper and contact printed from assembled 16mm film negative strips. A few composing cameras are used—some of European origin—and there is little doubt that for large volume work automatic composing cameras should be used for the composition of negatives of lengthy documents on single sheets of film. Most of the photography now, however, is done in 16mm microfilm cameras.

The largest producer is the Microcard Corporation, but there are several other organizations which have set up installations. Microcards are available of many

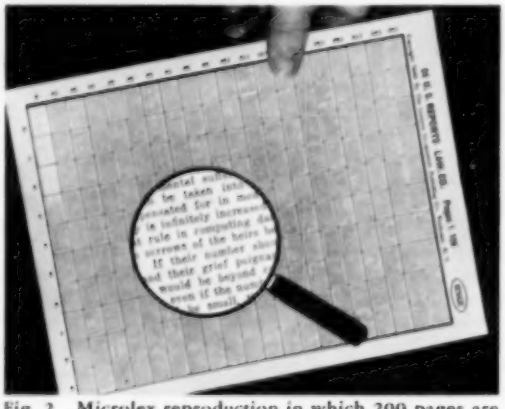

Fig. 2. Microlex reproduction in which 200 pages are reproduced on one $6^1/_2$- by $8^1/_2$-inch card.

extensive sets of scientific publications and patents. There is still uncertainty as to the proper function of the micro-opaque card, and in any case much depends on the availability of good readers at modest cost.

For several years, the Readex Microprint Corporation has put out large quantities of microreproductions of public documents printed by lithography on 6- by 9-inch cards with copies of 100 pages on a side.[10] Microlex Corporation is planning to publish reprints of law books on $6^1/_2$- by $8^1/_2$-inch cards with 200 pages of text on each side. (Figure 2.) So far, lithography has not proved adequate for this purpose, and photographic prints are preferred, contact printed from sheet negatives exposed in a composing camera of unique design, and mounted back to back.

A recent variation of the system known as Microstrip uses contact photographic paper strip prints from 16mm

Fig. 3. Diffusion transfer process—*b* paper support carrying emulsion *a* in which negative image is developed. On contact with the receiving sheet *c* undeveloped silver salts from *a* migrate to surface of *c*, and are reduced in the presence of nuclei to form a positive image.

negatives, the prints being provided with an adhesive for mounting on cards. Prints made at different times can be assembled on the cards and other entries can be added. The Picturesort Company also reproduces abstracts, drawings, etc., on cards to which microfilm strips can be attached.

A number of attempts have been made to interest people in miniature printing, that is, reproduction in which the text is just legible to the unaided eye, or in which a low magnification glass is needed for satisfactory reading. Such systems would result in a saving in publication space and therefore of library shelf space and presumably of printing costs. The merit in such reproduction is obvious, but, so far, it has not become popular. In an effort to save space without unduly impairing legibility, some experiments have been made here using an anamorphic system in the camera to compress the reproduction laterally or vertically up to 50 percent, retaining the full size in the other direction. The opinion of most of those who have seen the tests has been that they would prefer an over-all reduction to 50 percent.

Direct document reproduction to normal scale on photographic paper, which is done on a very large scale in the United States and more recently particularly with automatic continuous processing equipment, has in the past always produced a print with white characters on black background (Photostat, Rectigraph and Dexigraph systems). In order to obtain black characters on white, it was necessary to rephotograph the first copy. It would be desirable for most purposes to be able to produce black type on a white background in a single stage. This is now being done to a rapidly increasing extent as a result of the recent introduction of a paper of camera speed which gives positive prints on single stage development. It has been used by railway and steamship companies for making copies of waybills from which multiple copies may be further made by contact printing on diazo papers. With the introduction of modified continuous paper processing equipment, the uses of this type of paper are rapidly expanding.

A few years ago there was introduced another direct positive paper which gave reversal by the Herschel effect and which is used primarily for copying engineering drawings by contact and particularly for making intermediate positive prints for subsequent reproduction by the diazo process.

Although diazo-type printing processes are used extensively in the United States for direct engineering and document copies, the screened diazo-foil Retocee process apparently has not been widely used in the United States. Some attention has been paid to the production of duplicate negatives and duplicate positives on diazo-sensitized film, but the practice apparently is not very extensive.

Transfer Processes

The diffusion-transfer reversal processes have achieved considerable popularity in the United States. In particular, the adaptation worked out by Land and the Polaroid Corporation for producing a photograph directly in the camera in about a minute has found a variety of special uses including the copying of documents.[21] There are also several processes available on the market which appear to be related to those disclosed by Rott, Weyde, and others.[11,21] In these latter processes (e.g., Remington-Rand Transcopy, Apeco Auto-Stat and other systems), an image is developed in a sheet of paper and the silver salts in the undeveloped areas are transferred to a receiving paper coated with reducing nuclei where development of the transferred material takes place (Figure 3).

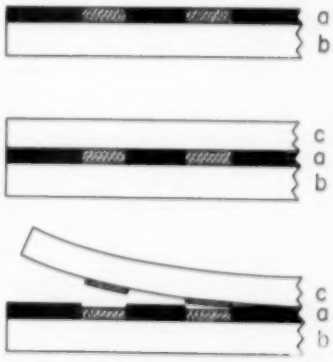

Fig. 4. Kodak Verifax System. A hardened negative image is developed in emulsion *a* on support *b*. Silver and dye are produced in unhardened areas which are transferred by contact to receiving sheet *c*.

In 1952 there was introduced a new type of transfer copying process known as the Kodak Verifax system. In this case, a paper carrying an unhardened emulsion, which also contains dye-forming components and the developing agent, is exposed and placed in an alkaline solution which brings about tanning development of the exposed areas. The negative is then put into contact with a receiving sheet of plain paper to which some of the unhardened layer is transferred by adhesion to give a positive of good density (Figure 4). Three good positives can usually be transferred from one original negative, and in some cases more copies have been pulled. Transfers can also be made to paper lithographic printing plates for multiple reproduction on office duplicating machines.

An interesting feature of the Kodak Verifax system lies in the incorporation of a nondiffusing developing agent in the emulsion, the requirement for developing being merely to soak the exposed paper in a solution of alkali.

Recent years have seen the introduction of photographic printing papers which can be handled in normal room illumination without fogging. They are generally coated with emulsions which have a high reciprocity failure, and merely require a high intensity for the printing exposure.

Rapid production of photographic copies frequently involves shortening the time required for processing the film or paper. Much study has been devoted to this,

and it has actually been possible to produce finished photographs in one second or less.

Rapid and Abbreviated Processing Methods

In rapid development, it is usual to increase the activity of the developer to shorten the developing time. This is done by increasing the alkalinity or adjusting the concentrations of the components to produce a more rapidly acting developer, raising the temperature, and other common devices.[12] Increased temperature is also used for shortening the time of fixing and washing, and special attention has been paid to rapid drying, in some instances the washing and drying being accelerated by use of papers which have low water absorption. Combined developing and fixing solutions, sometimes called "monobaths," have been much investigated with the object of shortening processing times,[13] but there are many objections to the systems so far studied, and they are very little used.

The rapid production of a print can be facilitated by what is called stabilizing instead of fixing and washing. The principle is to convert the undeveloped silver halide into stable colorless silver complexes. The common way of doing this is to use a bisulfite-hypo bath preferably applied to the emulsion side only.[12,14] The U. S. Army Signal Corps has a method of stabilization processing which uses a thiourea bath following development in amidol.[15] Stabilization systems lead to rapid print production because of the elimination of the normal fixing and prolonged washing. They do, however, give prints of reduced stability, although in normal files such prints have been kept for several years. To preserve stabilized prints, it is desirable to avoid high relative humidities and prolonged exposure to sunlight.

In the case of films, particularly if they are specially hardened, processing times have been materially shortened by raising the temperatures of the solutions to as much as 125 F.[12]

A porous platen processor which was originally developed in the United States[16] and has recently appeared on the English market is a convenient device for processing single sheets of paper which can be handled in room light, and many devices are being experimented with to simplify the handling of conventional photographic materials.

Non-Silver Processes

Although they are not photographic in the sense that they use silver halide emulsions, two processes which have come into use recently should be mentioned because they are intended for document reproduction. In one of these, known as Xerography,[17,18,19,21] a sheet of metal with a photoconducting coating is given a uniform positive electrostatic charge. It is then exposed and the electrical charge is conducted away in the exposed areas, leaving on the plate an electrostatic image which will attract a dry negatively charged black developing powder. This image in black powder can be transferred to a sheet of paper by contact and applying to the paper a positive electrical charge. After the powder image is transferred to the paper, it is fused in position by heating (Figure 5). Copying can be done in a contact printer, in a camera, and by enlargement, for instance, from microfilm negatives. The Xerographic image can also be transferred to offset paper plates for reproduction on small lithographic duplicating machines. Xerography has been used for reproducing among other subjects, printed documents, engineering drawings, catalogue cards, microfilm enlargements and transmitted images on cathode ray tubes.

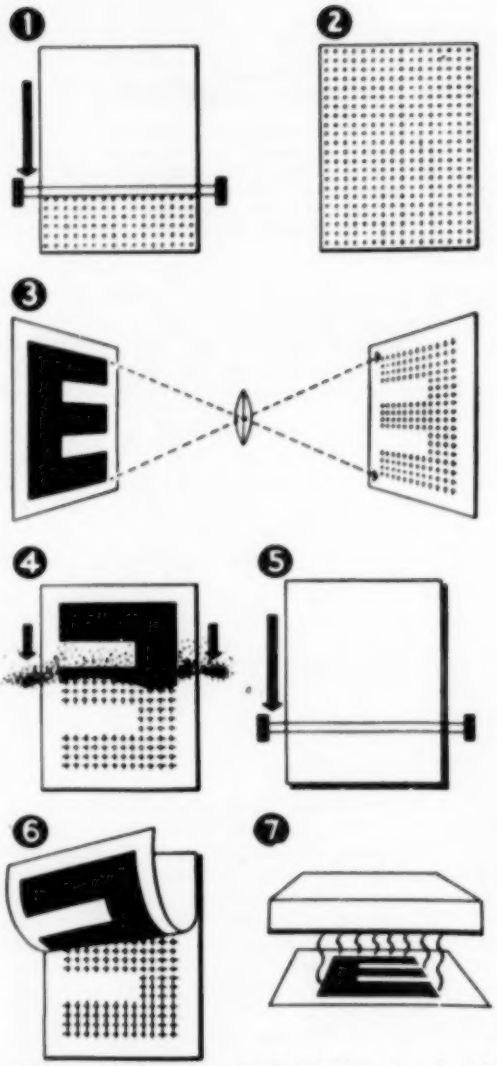

Fig. 5. Xerography. (1) Metal plate coated with photoconductive layer is charged electrically by a corona discharge. (2) Positively charged plate. (3) Image of copy projected on plate discharges plate in exposed areas. (4) Negatively charged powder adheres to residual positively charged image. (5) Paper is placed over plate and given positive charge. (6) Paper attracts powder from plate to give a positive image. (7) Powder is fused to paper by heat. (Credit: The Haloid Co.)

The other process, known as the Thermofax process,[20,21]

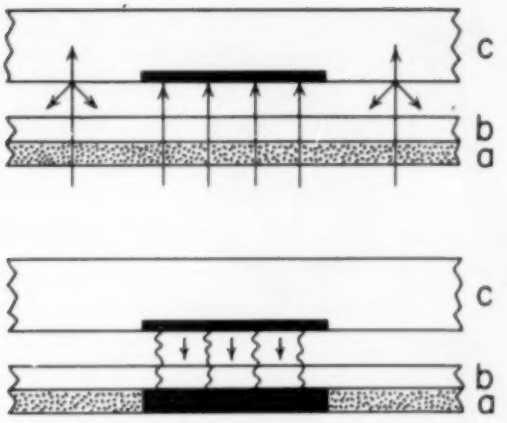

Fig. 6. Thermofax process. Heat passing through sensitive layer *a* on support *b* is absorbed by black type matter on copy *c*. Heat reradiated by black type produces visible change in sensitive layer *a*.

in its first form uses a thin white paper coated on the back with wax dyed dark blue. The document to be copied is placed in contact with this paper and exposed to infrared, usually by the reflex principle. The reradiation from the black printed type melts the wax, causing it to penetrate through the paper and so gives a reproduction of the type matter visible from the uncoated side of the sheet. In a later version the paper is white, but is treated with a material which turns black on irradiation by heat (Figure 6).

There is much activity in devising special reproduction systems such as the issue of lists of credit ratings or telephone directories which must be changed very frequently, selection and reproduction of information in card catalogues, and so on. Attempts are being made to apply the Corning Fotoform glass to the reproduction of documents through the intermediary of a photographic positive.

Microfilm and Microtext Readers

Whenever the merits of microreproduction on film or opaque cards are considered, the question of how to read the material is paramount, and many of the objections voiced against microreproduction are concerned with the readers. Although no reader will ever exist which satisfies all users, much thought is being given to the design of effective readers, and to a universal reader which will handle all forms of reduced photographic reproduction. In 1951, there were reported the results of a survey of hundreds of users made by the Document Research Unit of the Navy Research Section of the Library of Congress.[22] Most readers used microfilm, although there was a great increase in the use of microtext on cards. The majority preferred to view the image directly on the screen of the reader rather than on a horizontal surface, a wall, or a separate screen. Quite a number preferred a screen angle adjustment over a range from 45° to 80° to the horizontal. Most preferred an image size about 10 by 12 inches, a viewing distance of a foot, and the whole page to be seen at one time, and a fair percentage preferred some enlargement over the size of the original.

It seems to be generally agreed that use of readers involves more fatigue than reading original documents, and there are frequent complaints of fatigue on the part of people who use viewers in which the image is projected from behind onto a translucent screen. D. L. MacAdam in the Kodak Research Laboratories has made some studies in this field, although the results have not before been published. He feels that one of the main factors that determines fatigue in using certain readers is associated with the "hot spot." This spot, which is the concentration of illuminance in a narrow angle about the direct ray from the projector lens to the eye, may not be very apparent on casual inspection, but, if it is there, the observer tends to avoid it by excessive head and body movements or undergoes nervous tension in resisting the tendency for such movements.

The surrounding illumination is important for comfortable reading and to illuminate the working surface between the reader and the observer. It causes appreciable loss of contrast, although this does not appear to be a serious cause of fatigue in carefully lighted rooms. Fatigue is increased by external illumination of the screen by intense sources behind the observer and dark surroundings, which make the screen a source of glare, and it may also be increased by the scintillation sometimes observed.

Micro-image Quality Determinations

Practical and scientific study has been devoted to the factors determining the quality of micro-images. R. G. Rudd[23] has listed the factors which seem to be of practical significance in the case of microfilm images intended for enlargement onto paper, but they are also applicable to contact copying and to viewing in readers or by projection onto a screen. The important factors are:

1. High-quality lenses of high aperture and good definition, in precise focus, and free from flare light must be used. A common cause of poor quality is the introduction of flare by dirty lenses in the camera.

2. Films for microfilm negatives must have a compromise of high resolving power, good image sharpness, very fine grain, and reasonable speed. Very high contrast and short scale are frequently a disadvantage.

3. Exposure of negatives is critical. In general, the lower the contrast of the document, the less is the negative exposure; the higher the contrast of the original, the greater is the exposure. In addition to contrast (brightness range of the original), the thickness of the lines and their proximity to one another are of great significance. Overexposure tends to fill in the narrow portions of letters in the negative, requiring extra exposure for them in enlarging, and this results in spreading of the broader lines. Reduction of the exposure in printing to give best reproduction of large letters gives low density and low legibility in the fine lines. Underexposure in the negatives with appropriately lower exposure in enlarging gives low contrast prints with low legibility.

4. Finer dark lines have higher negative density than broader lines, and this is naturally more evident at

higher degrees of reduction. In the case of narrow white lines on a dark background, the negative density of the lines decreases as the line width gets narrower. The spreading of radiant energy into the shadow at the expense of that within the irradiated area can easily be shown by making microdensitometer traces of photographs of lines varying in width (Figure 7). The minimum density of the reproduction of black lines increases as the line width narrows, and the maximum density of the reproduction of white lines decreases as the line width gets narrower. It is evident the film and exposure for a document containing light and dark lines must be selected on the basis of a compromise. It has been suggested that the suitability of an emulsion for such copying should be evaluated in terms of a critical line width for which the density of the image of a white line on a black background equals that of the image of a black line on a white background.

5. The quality of reproduction is obviously dependent on the quality of the document copied, and in the case of typewritten and printed matter the density and clarity of the letters and the nature of the printed paper surface are of paramount importance (Figure 8).

In practice, for best negative quality from a variety of subjects, it is found best to classify documents in five broad categories of quality (according to line width and contrast) and assign a different camera exposure for each so that the negative densities are roughly the same for all documents. This means that all negatives in a roll can be printed at constant exposure to give uniform average high quality.

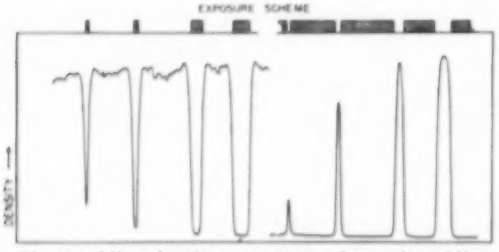

Fig. 7. Microdensitometer trace of negative of lines of varying width. Minimum density of reproduction of black lines increases as line width narrows; maximum density of reproduction of white lines decreases as line width narrows.

Standardization of Photographic Document Reproduction

A few years ago, the American Standards Association adopted three standards in the field of photographic reproduction of documents under the auspices of ASA Sectional Committee Z38 on Photography.[24] These dealt with specifications for microfilm readers (Z38.7.9-1946), reels for processed microfilms (Z38.7.17-1946), and standard practice for microfilms (Z38.7.8-1947). The Z38 program was reorganized in 1950 as a group of new sectional committees under a Photographic Standards Board, and in June, 1953, there was organized a Sectional Committee on Photographic Reproduction of Documents, PH 5, with subcommittees dealing with microtransparencies, micro-opaques, and documents readable without optical devices. The Committee was

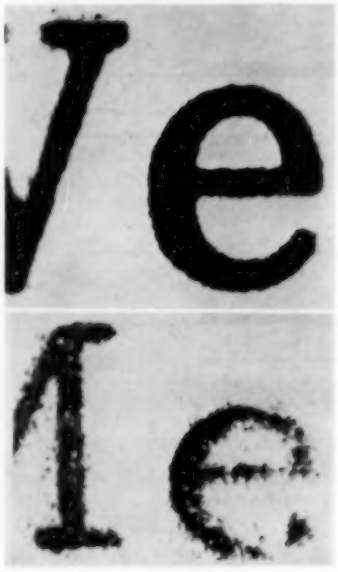

Fig. 8. Varying quality of typewriting. Both were typed on same machine, upper on special paper using an acetate sheet ribbon; lower on average-grade card using a woven cotton ribbon.

represented by Paul Arnold at the Paris, July, 1953, meeting of a Committee of Experts on Microfilm called in connection with the work of Technical Committee 46 on Documentation of the International Organization for Standardization (ISO).[25]

Document Reproductions for Archival Use

The factors determining the permanence of document reproductions for what is referred to as archival storage have been thoroughly studied. They have been published, and it can now be said that it is possible to make photographs which have the permanence of the paper or film support on which they are printed, and that the conditions under which they should be stored for maximum life have been soundly established.

Some people feel that all documents should be kept forever. Perish the thought. But who would accept the responsibility for the selection? Fortunately, the photographic technologist is only concerned with providing the means for copying the documents and making them available. The foregoing attempts to indicate some of the attitudes and techniques which have appeared in the United States in recent years.

Short Bibliography

1. O.E.E.C. (Organization for European Economic Co-operation). "Documentation Techniques in the U.S.A." O.E.E.C., Paris, 1951, 57 pp. Includes bibliographies.

2. Binkley, R. C., "Manual on Methods of Reproducing Research Materials.," Edwards Bros., Ann Arbor, Mich., 1936, 207 pp.

3. Tate, V. D., "Reflex and Photocopying." *The Complete Photographer*, Vol. 8, pp. 3086–3099, No. 8, 1943.

4. Holmes, D. C., "The Library of Congress Photoduplication Service." *Amer. Documentation*, Vol. 1, pp. 84–87, No. 2, Spring (April), 1950.

"Mechanical Methods of Enlargement Print Production and Related Processes in Use at the Library of Congress." *Amer. Documentation*, Vol. 2, pp. 216–219, No. 4, Fall (October), 1951.

5. Ellsworth, R. S., "New Horizons with Microfilm." *Amer. Documentation*, Vol. 2, pp. 221–228, No. 4, Fall (October), 1951.

6. Shaw, R. R., "The Rapid Selector." *J. Documentation*, Vol. 5, pp. 164–171, 1949.

"High Speed Intermittent Camera." *Amer. Documentation*, Vol. 1, pp. 194–196, No. 4, Fall (October), 1950.

"Management, Machines and the Bibliographic Problems of the Twentieth Century." In Shera, J. H., and Egan, M. E. (ed.), *Bibliographic Organization*, Univ. of Chicago Press, 1951.

"Machines and Bibliographical Problems of the Twentieth Century." In Ridenour, L. N., Shaw, R. R., and Hill, A. G., *Bibliography in an Age of Science*, Univ. of Illinois Press, 1951.

7. Rider, F., "The Scholar and the Future of the Research Library." New York, Hadham Press, 1944.

"Microcards vs. the Cost of Book Storage." *Amer. Documentation*, Vol. 2, pp. 39–44, No. 1, Winter (January), 1951.

8. Kuipers, J. W., "Microcards and Microfilm for a Central Reference File." *Ind. Eng. Chem.*, Vol. 42, pp. 1463–1467, August, 1950.

"Microcards and Documentation." *Amer. Documentation*, Vol. 2, pp. 89–95, No. 2, Spring (April), 1951. Selected bibliography.

9. Gray, D. E., "Practical Experience in Microfacsimile Publication." *Amer. Documentation*, Vol. 3, pp. 58–61, No. 1, Winter (January), 1952.

10. Boni, A., "Microprint." *Amer. Documentation*, Vol. 2, pp. 150–152, No. 3, Summer (August), 1951.

11. Varden, L. E., "Diffusion-Transfer Reversal Processes." Chapter 16 of C.B. Neblette, "Photography, Its Materials and Processes." Fifth Edn. New York, Van Nostrand, 1952, pp. 234–244. A comprehensive historical, practical and theoretical survey.

Hill, T. T., "Diffusion Transfer Processes as Applied to Photocopying." *Photog. Engineering*, Vol. 4, pp. 214–219, No. 4, 1953. Includes extensive bibliography.

12. Russell, H. D., "Procedures and Equipment for the Rapid Processing of Photographic Materials." *Photog. Engineering*, Vol. 2, pp. 136–147, No. 3, 1951.

13. Keelan, H. S., "Photographic Monobaths for Rapid Processing." *Photog. Engineering*, Vol. 4, pp. 157–161, No. 3, 1953.

14. Russell, H. D., Yackel, E. C., and Bruce, J. S., "Stabilization Processing of Films and Papers." *PSA Journal*, Vol. 16B (Phot. Sci. & Technique), pp. 59–62, August, 1950.

15. Levinos, S., and Bruner, W. C., "Stabilization Processing." *Photog. Engineering*, Vol. 2, pp. 148–160, No. 3, 1951.

16. Rudd, R. G., "A Porous-Platen Processor for Processing Photographic Materials in Room Light." *Phot. Sci. and Technique*, Vol. 1, Series 2, pp. 9–12, No. 1, February, 1954.

17. Schaffert, R. M., and Oughton, C. D., "Xerography: A New Principle of Photography and Graphic Reproduction." *J. Opt. Soc. Amer.*, Vol. 38, pp. 991–998, Dec., 1948; *PSA Journal*, Vol. 15, pp. 80–85, January, 1949.

18. Tate, V. D., "Xerography." *The Encyclopedia of Photography* (Morgan, W. D., Ed.), Vol. 10, pp. 3913–3918, 1949.

19. Clark, H. E., and Mott, G. R., "Negative-to-Positive Reproduction by Xerography." *Photog. Engineering*, Vol. 5, 1954. (Presented Soc. of Photog. Engineers, May 21, 1953.)

20. Carruthers, R. H., "Thermofax." *Amer. Documentation*, Vol. 1, pp. 212–213, No. 4, Fall (October), 1950.

21. Conrad, G. M., "Thermofax, Stenafax and Xerox." *Amer. Documentation*, Vol. 2, pp. 95–97, No. 2, Spring (April), 1951.

"New Methods of Reproduction, Publication, and the Design of Technical Reports." *Amer. Documentation*, Vol. 3, pp. 168–175, No. 3, Summer (August), 1952.

22. Conrad, G. M., "User Needs in a Microfacsimile Reader." *Amer. Documentation*, Vol. 2, pp. 201–204, No. 4, Fall (October), 1951.

23. Rudd, R. G., "Some Factors Influencing the Quality of Microfilm Images." *Proc. Second Annual Meeting National Microfilm Association*, New York, March 19–20, 1953.

24. American Standards:
Specifications for Microfilm Readers. Z38.7.9-1946.
Reels for Processed Microfilm. Z38.7.17-1946.
Practice for Microfilms. Z38.7.8-1947.

25. I.S.O. Organisation Internationale de Normalisation.
"Rapport sur la Réunion d'Experts Micro-Copies Paris-1 au 4 Juillet 1953." ISO/TC, 46/SC 1 (Secretariat 24), 42 F, Reproduction Documentaire. October, 1953.

MAKING AMERICAN STANDARDS EFFECTIVE

Carolyn Locher*

THE PHOTOGRAPHER who keeps up with "current events" in the trade journal or magazine of his choice has many times come across the symbol "ASA" and perhaps has wondered a little about the association behind the symbol.

From a modest beginning in 1918, the American Standards Association, Incorporated (ASA) has steadily grown until it now numbers among its members over 100 trade associations, technical societies, and consumer groups, as well as some 2300 company members, all with a common interest—voluntary standardization at a national level.

Through the "machinery" set up by the ASA, and the financial support of its members, voluntary national standards in the United States have become a reality.

The ASA is in effect a clearinghouse for standardization activities throughout the country and the projects approved as American Standards represent general agreement among manufacturers, dealers, and consumers, including the government. It is not until a consensus has been reached that the title "American Standard" can be conferred.

A standard is a solution of a recurring problem, and in the field of photography, many of these problems were difficult of solution. However, through the efforts of the representatives of the photographic industry who in 1938 met with others directly concerned and initiated the ASA project on photography, these problems have been gradually resolved.

It is seldom that a photographer consciously considers the fact that standardization is responsible for giving him greater satisfaction in the use of his camera. Standard dimensions for film, standard parts for cameras, standard processing procedures and the like all contribute to the ease with which he operates his camera, and the pleasure with which he views the finished product. One phase of the standardization program, technical though it is, touches him closely. Every time he buys a package of film, he profits by the reference in the instruction sheets to the "Exposure Index."

* American Standards Association, Incorporated, 70 East 45th Street, New York 17, New York. Received 2 March 1954.

35mm DIRECT POSITIVE FILM
SAVE! This unusual film enables you to make transparencies DIRECT from YOUR COLOR SLIDES without negatives. Film is Panchromatic with a daylight speed of 64 ASA, Tungsten 50ASA.
20-EXPOSURES
6 for 2.89—3 for 1.49
36-EXPOSURES
6 for 3.98—3 for 2.25
ANSCO COLOR RELOADS
20 EXP Daylight or Tungsten ASA 12 $1.50 Ea.
All fresh, Ansco quality film. Satisfaction guaranteed or money back. Please include 10c extra per order to cover postage and packing.
HI-SPEED COLOR FILM ASA 40*
Made for the Air Force by Eastman Kodak. Now made available to the general public by ... Photo. Same fine characteristics of Kodachrome but four times faster. Permits you to shoot in poor light—or stop down more for greater depth of field. And, saves you $ every time you use it. Each roll makes (6) SIX 20 exp cartridges. Processing available, but not included in price. Supply limited 35mm x 20 ft. roll.
3.95
Add 25c post and ins
* ASA 32 with filters. EK recommended speed for best results.

Fig. 1. Examples illustrating misuse of the American Standard Exposure Index and the symbol ASA, taken from three different dealer advertisements in the March 1954 issue of a popular photography magazine.

American Standard "Exposure Index"

At the first meetings of the committee responsible for the development of the "Exposure Index" it became apparent that there was an urgent need for standards which would provide a means for expressing to the public in a simple and reliable manner the sensitivity of films used for ordinary picture taking. The committee wanted standards that could be used by all, including manufacturers, dealers, publishers of technical magazines, and picture takers of all types from the casual snap-shot artist to the engineer or scientist who uses photographs for technical records.

To the special standards committee assigned this project the task seemed great indeed, for the problem was by no means new and many attempts to solve it had been made over the years in this country and abroad by individuals and organizations concerned. None of these met with universal success and it seemed impossible to produce an entirely satisfactory system for expressing photographic speed, much less a program correlating other elements as well.

The year 1948 saw essentially all of this particular program completed and the necessary standards well established in American photographic practice.

The American Standard Method for Determining Photographic Speed and Exposure Index, Z38.2.1–1947 (currently under revision as PH2.5 to include additional material), describes a means of measuring the sensitivity characteristic of film in terms directly related to picture-taking practice. A new testing method was set up in the standard and many important terms which had come to have a variety of meanings, such as "speed," were carefully defined. The standard also introduced a new concept, termed "Exposure Index," which is a value directly related to the exposure normally required for taking a picture. Exposure Indexes appear to be of greater use to most photographers than sensitometric speeds, which represent a more basic concept. The related American Standard for General-Purpose Photographic Exposure Meters (Photoelectric Type), Z38.2.6-1948, requires that Exposure Indexes be used for the "film settings" on exposure meters.

In 1942 an American Emergency Standard Photographic Exposure Computer, Z38.2.2–1942, was developed under ASA wartime procedure by a group of experts in the field. This standard was a direct result of a request to the ASA from the United States Navy for the preparation of a guide to exposure of sensitized film under various conditions all over the world for use by the Armed Services. Such favorable reports were received on the use of the Computer from the Armed Forces, and civilians who were unable to obtain photoelectric meters due to wartime shortages, the committee decided to revise it for peacetime use.

The new version of the Computer[1] (Z38.2.2–1949) presents to the photographer all the variables involved in good picture taking—weather, distance, time of year, time of day, sun and shade, film Exposure Index and even geographic latitude. For properly exposed pictures under all daylight conditions in any part of the world, it is merely necessary with ASA Exposure Computer to add together two numbers and then use the dial. Another improvement over the wartime edition is the additional information which has been included, which enables the photographer to use the Computer with reversal films intended for direct viewing and projection in both black-and-white and color. The wartime edition covered only black-and-white negative films.

Keeping American Standards Effective

A little-known service performed by the American Standards Association in connection with the use of these standards on film sensitivity is the close check the ASA keeps on the use of the term "Exposure Index" and the symbol "ASA" in published material. As stated in the scope of Z38.2.1–1947, the American Standard method of determining Speed and Exposure Index applies only to roll films, film packs, miniature camera films, sheet films and plates intended for the making of monochromatic, continuous-tone negatives for pictorial photography, exclusive of photography in the infrared. The standard does not apply to artificial light exposures or to process films and other graphic arts films and plates, and radiographic films. Likewise, the use of the designation "American Standard" or the initials "ASA" is prohibited should any factor be varied in the testing technique (that is, in the production of the density-log

[1] See "Correct Exposure for Every Latitude," J. W. McNair. Photographic Science and Technique, Vol. 17, No. 9 (September 1951) p. 96.

exposure curve). Following are excerpts from a few representative cases where the ASA has called attention to the unwitting misuse of the symbol and term in promotional material.

1. Several years ago it was noticed that a film carton for outdoor color film of the reversal type was being marketed under a label stating: "ASA Rating Daylight 10, 24 Exposures." The ASA called the distributor's attention to the fact that there is no such thing as an "ASA rating" for photographic film and it was not correct to use the initials "ASA" in connection either with a color film or a direct reversal film. It would be permissible to use the designation "Exposure Index," but the initials "ASA" should not be associated with that term in this instance. The distributor of the film thanked the ASA for the information supplied and agreed to discontinue the use of the cartons promptly and replace them with cartons giving the correct information.

2. In 1950, the announcement of a new photographic exposure computer was published with the statement—"Computer includes a table that lists ASA daylight and tungsten exposure indexes for all popular . . . . films"; The ASA pointed out to the organization which manufactured the computer that the American Standard Z38.2.1–1947 expressly restricts the use of the term "ASA Exposure Index" to data obtained in strict compliance with the standard. It further pointed out that the standard deals only with sensitometry using light of daylight quality. The term "Exposure Index," without the designation "ASA," however, could be used for tungsten ratings provided the standard was followed in all other respects.

3. Also in 1950 it was noticed that a roll film carton of a distributor stated—"ASA meter rating: 64 Daylight, 40 Tungsten." The ASA wrote to the distributor and directed his attention to the fact that no American Standard existed which covered "ASA Meter Ratings" and that the correct expression was "American Standard Exposure Index," or, if insufficient space was available on the carton, the shorter form—"ASA Exposure Index" could be used.

This particular distributor was especially grateful for the information supplied and expressed regret that a technical error had been made. He agreed to correct the cartons on the next printing.

4. In December 1952, attention of the editor of a popular photography magazine was called to misuse of the ASA symbol in connection with reversal type film and illumination other than daylight.

In this instance, and in additional instances involving other publications, the misuse was not in the advertising columns but in the editorial matter. As usual, the utmost cooperation was pledged in preventing recurrences and the ASA was thanked for its educational efforts leading to proper use of American Standards.

5. A midwest manufacturer misused the symbol ASA on an exposure calculator mounted on amateur motion picture cameras using reversible type films. First the symbol was incorrectly associated with the term "speed" when actually "Exposure Index" was intended. Later an incorrect use of the ASA symbol in connection with reversible films was averted by the timely advice of the American Standards Association.

6. Even the prominent manufacturers of photographic film have slipped occasionally and published incorrect references to ASA Exposure Indexes due to overzealous copy writers in their advertising departments and the efforts of agency personnel who are unfamiliar with the American Standard Z38.2.1.

Fig. 2. These two dealer advertisements from the November 1953 issue of a U. S. camera magazine illustrate some violations of the American Standard Method for Determining Photographic Speed and Exposure Index. All four ASA numbers are manifestly the product of "pen and pencil" rating rather than sensitometric laboratory tests. The ASA symbol is used in four different ways that are expressly prohibited by the American Standard: (1) without further identification as ASA Speed or ASA Exposure Index, though the latter is intimated, (2) applied to color negative film though the standard is restricted to monochrome materials, (3) applied to reversal film though the standard is restricted to negative, (4) used with tungsten illumination though the standard is restricted to light of daylight quality. The unauthorized term "rating" is associated with the symbol ASA though the standard defines only ASA Speed and ASA Exposure Index. The figure 300 ASA is listed though the American Standard Exposure Index scale does not include any such figure and requires that rounded-off numbers be used in a specified series.

Other similar cases continue to cross the desk of the technical director of the American Standards Association. When these misuses of the American Standards or the registered initials "ASA" are pointed out, there always is noticed a real willingness to cooperate in the correct use of American Standards.

It is hoped that as the years pass more and more of the individuals and firms concerned with progress in photography will avail themselves of the services of the ASA, extending the use of standards which are voluntary, not mandatory, and which are so representative of the American way of life.

REPORT TO THE PSA STANDARDS COMMITTEE

H. R. Sprentall*

During 1953 two proposals submitted by PH2 have become American Standards. One of these, titled "Method for Determining Exposure Guide Numbers for Photographic Lamps, PH2.4-1953," is available in printed form while the other, "Method for Determining the Relative Photographic Efficiency of Illuminants, PH2.3-1953," is now being printed.

In its present form the Photographic Efficiency standard applies only to continuously burning light sources. However, further work has led to the development of a procedure for determining the efficiency of momentary light sources such as flash lamps, and it is proposed to incorporate this procedure in a revision of PH2.3. This proposed revision is in the hands of the members of PH2 for letter ballot.

Revisions of two older standards have been prepared also. The first of these is the Speed and Exposure Index standard, originally issued in 1943 and revised in 1946 and in 1947. The current version, Z38.2.1-1947, has been re-edited to take account of minor improvements suggested by the standards bodies of other nations, and to bring the terminology up to date. This proposed revision has been accepted by PH2 and is now being considered by the sponsor (ASA Photographic Standards Board). The second is an editorial revision of the Method for Determining Spectral-Sensitivity Indexes and Group Numbers, Z38.2.4-1946. This revision has been circulated to PH2 members for letter ballot.

Several other proposals are under consideration in the nine active subcommittees of PH2. Work is progressing well on drafts for the sensitometric exposing of color films, for measuring and classifying flash lamps, and for sensitometric test methods for medical and industrial types of x-ray film.

The subcommittees are also studying methods for measuring reflection density, illuminants for viewing color transparencies and prints, a test method for films used for measuring the extent of exposure of personnel to penetrating radiation, film speed at short exposure times, and the general subject of nomenclature in the field of sensitometry.

In addition, members of PH2 are working on revisions of the Photographic Exposure Computer (Z38.2.2-1949), Diffuse Transmission Density (Z38.2.5-1946), and Photoelectric Exposure Meter (Z38.2.6-1948) standards. The Committee will be glad to undertake any additional standards projects within its field of endeavour that may be requested by PSA members.

The Committee is continuing to follow with interest the progress of the Draft International Recommendations for Speed and Exposure Index and for Diffuse Transmission Densities. These Draft Recommendations are based on the corresponding American Standards, and were proposed for international consideration by ASA. They have been accepted by the Technical Committee on Still Photography of the International Organization for Standardization (ISO/TC 42), and have been submitted to the ISO Council for final action.

* Kodak Park Works, Rochester 4, New York. Mr. Sprentall, who represents the Photographic Society of America on ASA Sectional Committee PH2, is Chairman of that Committee.

BETTER EXPOSURE GUIDE NUMBERS

R. E. Farnham, FPSA*

ABSTRACT

New ASA Standard for determining exposure guide numbers (PH2.4-1953) clarifies this long used device and should remove many of the inconsistencies that have bothered photographers. The following article discusses the mathematical approach to the problem and the variety of factors involved.

A list of the various elements that must be observed in order to obtain a "properly" exposed negative is one of imposing length. It might include the following:

1. Exposure index and color sensitivity of the film.
2. Power of the light source.
3. Distance of the light source from the subject.
4. Effect of the reflector used with the light source.
5. Quality or spectral composition of the light.
6. Lens aperture setting.
7. Speed of the shutter.
8. Influence of development.
9. The photographer's own judgement of what constitutes a properly exposed negative.

It is not possible for either the film manufacturer or the maker of photographic light sources to provide exposure information that will always satisfy item 9. Insofar as item 8 is concerned, the best the film or light source manufacturer can do is to see that his exposure data makes available satisfactory negatives with the customary development procedures.

This leaves seven exposure elements that must be given consideration before taking a picture. In the case

* General Electric Company, Nela Park, Cleveland, Ohio. Mr. Farnham is Chairman of ASA Subcommittee PH 2-5 (Photographic Illuminants).

of a steady or continuously burning light source, an exposure meter provides the answer for items 2, 3, 4, and 5, and it only remains for the photographer to apply items 1, 6, and 7 to his exposure meter calculator to give him all the necessary information to take his picture.

The introduction of photoflash lamps in 1930 and their immediate general acceptance, created a real problem of providing accurate exposure information. Exposure meters were useless. Those experts who set their exposures from the brightness of the image on the ground glass were helpless. The human eye was of no use in gauging the amount of light available from a flashbulb. Consequently early exposure information published by flashbulb manufacturers read something like this, "for film speeds of from 12 to 16 and number 'X' photoflash lamp with open flash, use f/14 at 6 ft.; f/7 at 12 ft., etc." All very well for picture taking under the conditions outlined, but what to do with other film speeds, and other distances. Mental gymnastics involving squares and square roots were required. Obviously simplification of a high order was called for.

It was realized that a person setting out to take some flash pictures started with film of a particular exposure index, with flash bulbs of a particular size or light power, likewise reflector and an inclination to stick to "open flash" or perhaps a 1/200-second shutter setting. If such were the case, all that remained for him to do was to set his lens aperture in accordance with the distance from the lamp which is usually at or near the camera. It was soon found possible to provide a single number which represented the product of the distance from the flashbulb to the subject and the lens aperture setting using the "f" system, since they are inversely related. The value of this "guide number" would be governed by the exposure index of the film, the power of the flashbulb, including its light quality, and the shutter speed setting.

Thus our photographer, starting out on a picture-taking expedition, has only to look up the guide number for the film, flashbulb (and reflector) that he has with him. Upon getting set for his picture, he notes that the subject is 8 feet away and 8 divided into this guide number, which let us say is 64, gives him an aperture setting of f/8.

The Original Guide Numbers

The first guide numbers, published in April, 1941, were obtained by means of trial exposures using various films, flash bulbs, shutter speed settings and noting the aperture openings and distances. Guide numbers for other exposure conditions were obtained by computation from these experimentally determined values.

These guide numbers have played an important part in the popularity of flash pictures because they eliminated much of the guess-work. Unfortunately there were troubles; guide numbers published by film manufacturers often disagreed with those put out by the bulb makers. Guide numbers for similar powered flashbulbs of two different manufacturers for the same film sometimes did not jibe. The reasons were soon apparent. Some were obtained with a polished reflector, others with a diffuse finish reflector. Size of reflector often influenced the results, and finally, there was no agreement as to the density to which the film would be exposed. What was the poor photographer to do? His film carton might give him one value and the flashbulb bulb sleeve might show another.

Here was an excellent opportunity for the American Standards Association, through its photographic sectional committees, to establish a standardized procedure for determining guide numbers. The writing of such a standard involved the cooperation of all film manufacturers together with the several manufacturers of flash lamps. There were two general procedures which could have been followed: (1) The actual taking of photographs in a carefully standardized room with a special camera having a calibrated shutter and aperture adjustment; (2) The development of a mathematical formula which included all the usual variables and to which the flash lamp output, the film exposure index and a reflector factor could be inserted and a guide number arrived at.

The first method presented a pretty difficult problem in specifying room conditions, colors, etc., and obtaining a suitable laboratory camera. Obviously many samples of films and lamps would have to be used.

The Committee was fortunate in having available Messrs. Jones and Condit's very comprehensive paper, "Brightness Scale of Exterior Scenes and the Computation of Correct Photographic Exposure."* Only slight modification of these data were necessary to adapt them to interior scenes and artificial light sources. Accurate film exposure indexes are available through ASA Standard Method for Determining Photographic Speed and Exposure Index (Z38.2.1-1947). Photometric laboratories have well established methods of measuring the light distribution of reflectors.

American Standard Guide Numbers

Weighed against the complicated method of test pictures, it was a comparatively simple problem to develop a mathematical method of determining guide numbers, which have subsequently been verified by field trials. This has been made available in the recently published "American Standard Method for Determining Exposure Guide Numbers for Photographic Lamps" PH.2.4-1953, available from the American Standards Association, Incorporated, 70 East Forty-Fifth Street, New York 17, New York.

The final paragraph of the standard concludes as follows:

$$G_n = \sqrt{.005LtMS}$$ in which

- G_n = Guide Number.
- L = light output from the source in lumens.
- t = time of exposure in seconds.
- M = The reflector factor, a number representing the gain in effectiveness for a lamp-reflector combination over a bare lamp.
- S = The speed of the film according to the ASA rating for that type of light source.

The constant .005 or 1/200 welds these four quantities together and its value has been governed by:

* Journal of the Optical Society of America, Vol. 31, No. 11 (November, 1941).

1. A safety factor.
2. Development of the film.
3. Reflectance of the subject.
4. Lighting composition.
5. Nature of the subject environment.
6. Transmission of the lens.
7. Effect of finite object distance.
8. Cos^4 effect.
9. Vignetting by the lens barrel.

Since L represents lamp lumens and t, time of exposure, the guide number formula is applicable to steady burning sources as well as flash sources whose output values are expressed as lumen-seconds (Lt). Knowing the candlepower distribution of the reflector, the standard outlines in its appendix, the method of arriving at the reflector factor, which weighs the importance of the various areas of the picture.

When flashbulbs are used with the shutter operating at speeds greater than 1/25 seconds, part of the flash is cut off and a correction must be applied to the value Lt. The method of obtaining this correction from the light-time curves published by the lamp manufacturers is likewise given in the appendix.

The importance of this standard to both film and flashbulb manufacturers was demonstrated by their immediate use of the guide number formula by manufacturers in both categories even at the time it was being circulated for general comment and approval, and before its final approval as an American Standard.

The final formula is really so simple that the mathematically inclined can easily remember it and make up their own guide numbers. The familiar GE #5 photoflash lamp has a rated output of 16,000 lumen-seconds. The usual small reflector of the matte finish type has a reflector factor of 5. (Polished type 8.) There is shown on the data for Ansco's Plenachrome film, for example, the speed rating of 25 for tungsten illumination. Applying these values to the guide number formula:

$$Gn = \sqrt{.005 \times 16000 \times 5 \times 25} = 100$$

As mentioned earlier, the guide number formula is equally applicable to steady burning sources such as photofloods. For example, the No. 1 photoflood has a light output of 8500 lumens and if you choose to use a 1/5 second exposure, the term Lt of the formula will be 1700. Likewise guide numbers for electronic flash can be obtained in the same way. The reflector factors will of course be different and no correction for high shutter speeds need be made, since the entire flash takes place within the opening of the fastest shutter.

If two lamps are to be used, one on each side of the camera, the L value will of course be doubled and this amounts to a 40 per cent increase in the guide number. In other words, when using two lamps of the same power and at the same distance, multiply the guide number for one lamp by 1.4 (i. e., $\sqrt{2}$).

The adoption of a standard procedure for obtaining guide numbers is another example of the many and varied activities, fostered by the American Standards Association, in which manufacturers and distributors unite with consumer representatives and experts having only a general interest in the subject to help photographers, both amateur and professional, obtain better pictures.

THE ACTIVITY OF PHOTOGRAPHIC RESEARCHES IN JAPAN

SHINNOSUKE FUKUSHIMA*

The influences of the Pacific War on the development and activity of the photographic science have been little in Japan. Damage of the photographic institutes and factories was rather small (except two representative colleges) as they are mainly located in the suburbs and escaped from the destruction of air raids. But the economical conditions due to the confusion of the social system after the War and the lack of a constant supply of modern instruments, especially the difficulty of communication with foreign countries made the researchers stop their work for 2 or 3 years after the armistice. The controlled price and sales quota of films continued as late as 1950. Finally, however, the Peace Conference and the general stability of the price index showed signs of restoration in Japan. This year, the industrial production of photographic materials reached as high as standard which was recorded in the year 1940.

The educational institutions of scientific photography in Japan are somewhat fewer in number as compared with other professional educational organs. There are lecture chairs in the two national universities, two colleges for professional education and two or three annual summer schools for general photography. Researches are made by the professors of the above organs and mainly by the young men of research laboratories which belong to the manufacturing companies of the photographic sensitive materials. Under the conditions above-mentioned, let me introduce the activities of photographic researches in Japan.

There is a group of men who are the followers of Prof. Kameyama, now the president of "Science Council of Japan" and also the ex-president of this society. The aim of their work is to account for the reaction mechanism of chemical sensitizing materials and its adsorption to silver halide surface by means of electro-chemical sensitizing materials and its adsorption to silver halide surface by means of electrochemical methods. Some groups are trying to account theoretically for the phenomena of various anomalous effects of sensitizing. At the Research Laboratory, Fuji Photo Film Co., Ltd., S. Fujisawa and E. Mizuki are making their effort to explain the mechanism of latent image formation and chemical sensitizing by means of precise experiments on the failure of the reciprocity law. The details of their work will be published in this Bulletin.

There are cumulative researches on the ripening inhibitor contained in the photographic gelatin that was in very short supply in Japan, as an industrial raw material during the War. The researches were continued from 1941 to 1952 and thirty or

* President, The Society of Scientific Photography of Japan, 1 Nihonbashi Muromachi 3 Chome, Chuoku, Tokyo, Japan. Reprinted by permission from December 1952 issue Bulletin of The Society of Scientific Photography of Japan.

more members engaged in them. Natural and artificial ripening inhibitors, including known and unknown constitutions, were tested for bromide emulsion, and, especially in the latter, more than 130 inhibitors of probable constitutions containing nitrogen and sulphur were synthesized. A part of these results will be presented to the International Congress of Photography 1953. We are satisfied with the discovery of some excellent inhibitors by these researches, for instance, Vitamine B1 and Penicilline G and their derivatives and furthermore a convenient process of testing the inhibiting power of the substances in question by the silver potential titration of the fog inhibitors.

An electron microscope cinematograph of crystal dealing with the change of silver salt under exposure was successfully made by M. Tajima of Research Laboratory, Fuji Photo Film Co., Ltd. Gelatin casted optical wedges of good neutrality which are generally used in this country for sensitometry were made by the author. An ingenious manufacturing process of silver halide emulsion continuously by mixing and overflowing followed by washing was tried by Prof. Kikuchi and M. Ohshima with success. Another process of manufacturing printing paper improved by T. Yano of Mitsubishi Paper Mill Co., is a new kind of paper in which polyvinyl alcohol is used as a vehicle instead of gelatin. This photographic paper will be on the market during this year.

We will now glimpse into the industrial production. There are three kinds of color films that are on the market. Two of them are without coupler in the film and another is the film containing coupler, i.e., Fujicolor film, Sakura color film and Oriental color film. The former two are used for color movies.

More than 3 million dollars worth of cameras and lenses including accessories were manufactured during 1951 and some of them were exported to U.S.A. The 35mm Leica type camera fitted with f/1.4 lens is contained in the above exported cameras. We are glad to say that this camera, which was rather inferior in the past, is now a first class camera.

In concluding, though the activities of photographic researches and the development of photographic technics in Japan were not fully communicated to foreign countries in the past because of the difficulty of language, we hope that in the future, through this Bulletin we will be an intermediator to the foreigners so far as the inquiries of details of researches in Japan are concerned.

The Society of Scientific Photography of Japan was founded in February 1926 and now numbers 729 members. Its journal is published quarterly in Japanese, each issue containing 4–5 original papers, reviews and proceedings. It is published annually in English, containing original papers. From Vol. 14 No. 4, the Japanese edition will contain the English abstracts of content. Up to Vol. 12, the English edition No. 1 contained abstracts of several reports. Dr. Akira Sasai of the faculty of Engineering, Chiba University is Chief Editor of the quarterly J. Soc. Sci. Phot. Japan, and the annual Bull. Soc. Sci. Phot. Japan.

The Society holds a General meeting each year in May, monthly meetings 8 times a year, original report meeting twice a year, public lecture meeting thrice a year, and a dinner party on the new year.

The membership is composed of 53% research workers and engineers, and 10% professors and scientists.

MECHANISMS OF COLOR-SENSITIZATION

Lester Horwitz*

WITHIN the framework of the various steps postulated in the formation of a latent image, a sensitizing dye cooperates to make the silver halide emulsion responsive to lower energy stimuli. It is by the interplay of several competing actions that one can hope to explain the phenomena observed.

Roughly, latent image formation takes place by a series of steps; the first being the impingement of a photon of light on the silver halide emulsion resulting, directly or as a consequence, in the elevation of an electron into a mobile state. The second step results when the electron mobility is stopped by a suitable energy sink and is then available for the third step. In this last step, the electron combines with a silver ion. Overall, there occurs the formation of neutral silver and halogen atoms by the transfer of an electron; the energy for transfer being supplied by the impinging radiation on exposure of the silver halide emulsion.

In discussing the role of sensitizing dyes in the above scheme, attention will be called to absorption, photoconductivity, aggregation, and structure of these dyes. Also, the action of desensitizing dyes and the phenomenon of desensitization by sensitizing dyes will be viewed. Particular attention will be paid to the overall fact that sensitizing dyes permit the photographic process to proceed under conditions of lower energy activation.

* Ansco Research Laboratories, Binghamton, New York. Received 8 March 1954.

Adsorption of the Sensitizing Dye on the Photographic Emulsion

Adsorption of a sensitizing dye to the silver halide crystal in an emulsion binds the dye to the crystal. In many instances extended resonance interaction among many dye molecules results from adsorption. The forces in the crystal to which the dye is attracted occur at regularly spaced intervals. As a result, when adsorbed as a monolayer, the dye molecules are lined up in juxtaposition one to another with the plane of each dye molecule parallel to the plane of the other dye molecules on the crystal surface. Such factors as these are conducive to a special type of resonance. The unsaturation electrons belonging to an individual dye molecule interact with the unsaturation electrons belonging to the many other individual dye molecules on the crystal surface. In this manner the many dye molecules bond together to form an aggregate, losing their individuality. It should be mentioned that many excellent sensitizing dyes do not exhibit any measurable interaction of their unsaturation electrons when adsorbed on silver halide or at any other time. When the unsaturation (π) elec-

trons interact the dye molecules can bind together and sensitize the emulsion as an aggregate or polymer.† The forces for aggregation of dye molecules are probably the same as those responsible for the very extensive molecular compound formation known to exist between aromatic molecules. The role played by adsorption in binding a sensitizing dye to the silver halide crystal, so that energy transfers between dye and crystal can take place, will be considered, also the additional part that adsorption can play in facilitating dye aggregation.

For any cooperation between the sensitizing dye and the silver halide in the photographic emulsion to take place, it becomes apparent that the two entities must become spatially adjoined‡. Spectral regions to which the emulsion becomes sensitized generally correspond to the absorption range of the dye adsorbed on the crystal; this range being towards the longer wavelength of the absorption of dye in alcohol or dilute aqueous solution. The majority of practical sensitizing dyes are cationic in nature and it is only to be expected that they will be electrostatically attracted to those bromide anions externally located in the silver halide lattice. Of course, the merocyanines, being uncharged, are adsorbed by virtue of their polar nature alone. In the case of certain merocyanines, West, Carroll and Whitcomb, who have extensively studied the adsorption characteristics of sensitizing dyes, postulate a linkage between the silver cation of the lattice and suitable electronegative atoms of the dye.[1] In general, the adsorption isotherm curves are of the Langmuir or, in some cases, Freundlich forms. They do not in all cases represent equilibria curves. Most adsorbed dyes can be displaced, however, by other strongly adsorbed substances, such as thiourea, and at least some are displaced by gelatin. Even rather strongly adsorbed dye molecules can wander from one grain to another in mixed emulsions. (Figure 1).

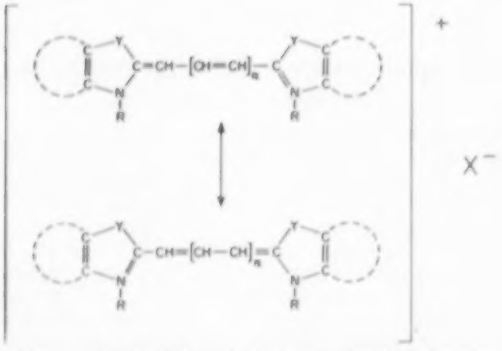

Fig. 1. General formula for a cyanine dye showing two of the canonical structures which contribute to the resonance hybrid. (Y may be —CH=CH— or some hetero-atom and n may have the values 0, 1, 2, 3).

† Perhaps the term aggregate is to be preferred since the effect is a concentration phenomenon. In this connection both terms have been used interchangeably.

‡ Care must be taken to distinguish clearly between the energy the dye acquires from irradiation (absorption) and the energy with which the dye clings to the silver halide grain (adsorption).

Fig. 2. Paracyclophanes. At proper values of m and n the π-orbital electrons of the benzene rings overlap, causing changes in spectral absorption characteristics (for ultraviolet and infrared).

As a result of the investigations initiated by Sheppard and co-workers[2,3,4] the cyanine dye, adsorbed onto the grain of the silver halide emulsion, is believed to be stacked with the plane of each dye molecule parallel one to another. In this way the silver halide crystal is covered by a monolayer of dye, each dye molecule some 4.6 A one from the other. The positive pole of the dye is oriented toward the crystal. From the magnitude of the heats of adsorption (10–12 Kcal. per mole for the first addition of well adsorbed cyanine dyes) it can be seen that the energy of adsorption lies somewhere between that of van der Waals and electrostatic forces.[1] Most likely both types are in play.

Certain aspects of adsorption can be correlated with the sensitization of particular cyanine dyes. There remains, nevertheless, no general relationship between adsorbability and efficiency of sensitization. Dyes which are non-planar are generally more poorly adsorbed. This is attributed to the greater distance over which the attractive forces between the non-planar dye and the silver halide crystal must operate. Non-planarity will restrict the freedom of motion or non-localization of the unsaturation or π electrons. This will diminish the van der Waals forces available for adsorption.[5] However, the poor adsorption of non-planar dyes does not completely account for their poor sensitizing qualities. It is only when the ability of the planar and non-planar dyes to hand over their energies to the crystal, to be used in the photographic process, is considered that one can understand the essential differences. Investigations have further disclosed that some non-planar dyes can be supersensitized and converted into more efficient dyes. The supersensitizers need not necessarily themselves be effective optical sensitizers nor absorb in the same spectral range as the sensitizer for the photographic process. This increased efficiency is not related to a increased energy of adsorption. Rather, it is an increased efficiency of energy transfer to the silver halide crystal that probably explains the process of supersensitization of non-planar dyes.

Consider the interaction of the unsaturation electrons of one molecule with the unsaturation electrons of other molecules (overlap of π orbitals). London has indicated that in elongated conjugated systems, such as are found in cyanine dyes, the unsaturation electrons belonging to the various molecules interact over greater distances than those usually associated with van der Waals forces.[5] A most satisfactory study of such interaction of unsaturated centers in molecules whose geometry is known is that of Cram and Steinberg.[6] These workers prepared paracyclophanes in which two un-

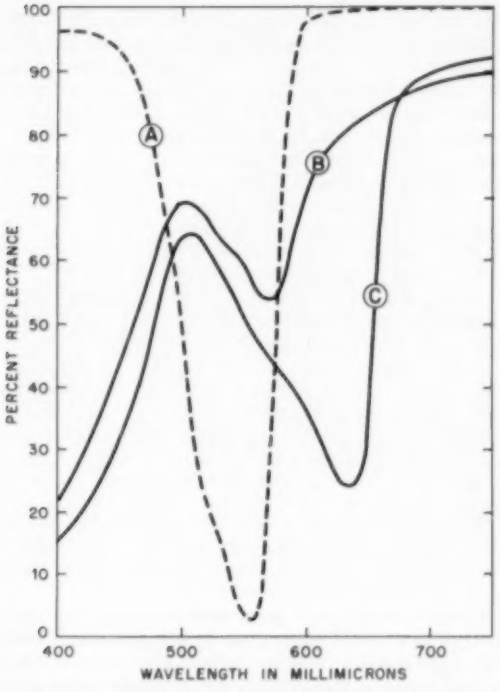

Fig. 3. Absorption of a cyanine dye (A) is plotted as a transmission curve for comparison with the absorption curve for the same dye when it is adsorbed onto the silver halide grain (B) and curve C, which is a cyanine dye absorbing in solution—as in Curve A, but absorbing when on the silver halide grain as a polymer. Note the shift of C to a much longer wavelength than is the case with the monomeric type dye shown in Curve B; also the narrow and more intense absorption band.

saturated benzene groups are fixed within the same molecule as parts of a large macrocyclic structure. The distances separating the benzene rings can be varied by varying the number of methylene groups in the macrocycle. When the distances between the benzene rings are small the π electron orbitals of the benzenes of the macrocycle can overlap and corresponding changes in the spectra of the compounds are observed when compared to the absorption characteristics of open chain analogs. The adsorption of a dye to a silver halide lattice may be viewed as a means of fixing the geometric relationship of the dye molecules one to another. When conditions are favorable, as is the case for many cyanine dyes, the unsaturated center of one dye molecule can interact with the unsaturated centers of many of the other dye molecules. Thus, many individual dye molecules are bound together as an aggregate. What is observed is a modification of the interaction of the unsaturation electrons of individual dye molecules (monomers) with light. The absorption bands characteristic of the monomer are diminished and there appears an absorption band attributed to a large number of dye molecules absorbing as an aggregate (polymer).

From the foregoing considerations it should be expected that a cyanine dye which aggregates can theoretically exhibit three different types of absorption when irradiated with polarized light. These separate characteristic absorptions are functions of electronic transitions in three dimensions. Scheibe has demonstrated this to be the case with pseudocyanine iodide.[7] A mixed crystal of quinaldine ethiodide and this dye was isolated from alcohol. In this manner the dye ions in the crystal were parallel one to another. Irradiation by polarized light whose direction of polarization (electric vector) was roughly parallel to the plane of the dye molecule (i.e., parallel to the length of the conjugated chain) caused absorption at 5300 A. When the light vector was vertical to the plane of the molecule only a weak and modified absorption of the dye at 4900 A occurred. These absorptions are characteristic of electronic transitions of monomeric dye; a transition (5300 A) in the long x axis of the planar dye molecule and another transition (4900 A) in the y axis. In the dimer the y axis transition appears to be intensified. Now, when the electric vector of the polarized light was parallel to the thread of the polymer (z axis) a new intense and narrow absorption band at a longer wave-length (5730 A) appeared; corresponding to absorption of light by the polymer. The polymer also exhibited a fluorescence band which is noteworthy in that this is the only type of complex molecule, so far as is known, having a fluorescence band and absorption band coinciding in position and half-width. As indicated, the electric vector of the light exciting electronic transitions through the axis of the polymer is perpendicular to the plane of each individual dye molecule making up the polymer. The very narrow polymer absorption band indicates that this electronic transition is not coupled with vibrational and rotational levels to any great extent. Nor is all the energy absorbed by the polymer easily transferred to the silver halide crystal. This is evidenced by the fact that the polymer exhibits resonance fluorescence. Energy emitted as fluorescence (by the dye) is lost to the photographic process. Monomeric dyes have wider absorption bands (indicating coupling with vibrational and rotational levels), but they also transfer the energy they absorb

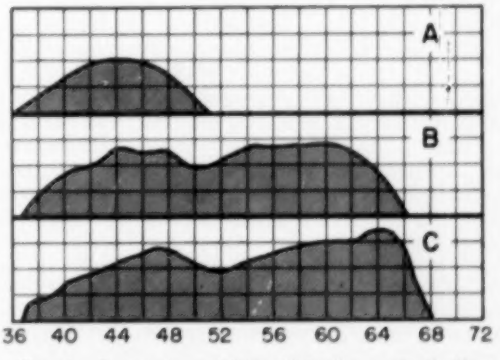

Fig. 4. Spectral sensitivity (A) of a normal silver bromide emulsion, (B) the same emulsion sensitized by a monomeric type dye having an absorption curve like Fig. 3B, and, (C) the same emulsion sensitized by a polymeric type dye having an absorption curve like Fig. 3C.

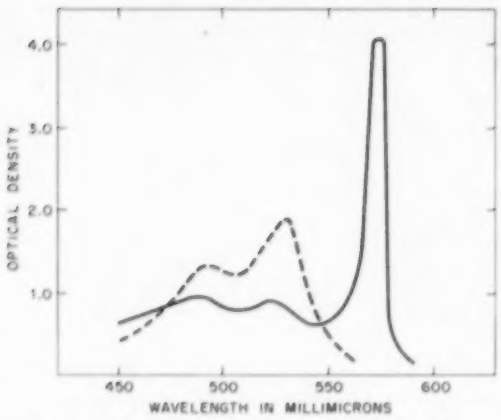

Fig. 5. Absorption of pseudocyanine in solution. The polymerised dye shows a sharply-defined, strongly absorbing band around 560 millimicrons. The dye in dilute solution (monomer), shown by the dotted line, has its maximum at 530 millimicrons.

more efficiently than do dye polymers to the silver halide crystal. A method of increasing the efficiency of energy transfer from dye to crystal is termed supersensitization. As will be seen later, supersensitization is most successfully applied to dyes which aggregate. With the supersensitization of a dye aggregate the energy photographically lost as fluorescence is transferred to the silver halide crystal; the fluorescence is quenched.

The preceding aspects of adsorption play a role in the usefulness of cyanine dyes as photographic sensitizers. The study of aqueous solutions of pseudocyanine chloride by Sheppard,[8] Scheibe[9] and Jelley[10] demonstrated that as the dye became more concentrated (0.01 M) the viscosity of the solution began to increase until a jelly was obtained. This jelly displayed fluorescence and absorbed in a new sharp and very intense band at much longer wavelength regions than its absorption in dilute solution. This longer wavelength absorption (called J-band) of the concentrated solution of pseudocyanine chloride was correlated with its sensitization of the silver halide emulsion. In this state, the bands of this dye observed in dilute solution are depressed. The sensitization of an emulsion of the kind displayed by pseudocyanine chloride, extending as it does even further out to the red than would be predicted from its absorption band in dilute aqueous solution, is called sensitization of the second type or second order sensitization. It is only as a fortuity that solubility characteristics allow this longer wavelength absorption band, attributed to a property of the dye in a polymerized form, to be observed in the case of concentrated solutions of pseudocyanine chloride. But this long wavelength maximum is prominently exhibited in the sensitized spectra of many other carbocyanine dyes which are insufficiently soluble in water or alcohol to achieve the minimum critical concentration needed to aggregate into a polymer. The addition of inorganic salts to these dyes in aqueous solution can frequently induce the appearance of these maxima in the long wavelength regions, which correspond to the sensitizing maxima characteristics of these dyes in the emulsion.[11] What happens is that polymerization of certain dyes is achieved in their adsorption to the crystal surface even in cases where solubility characteristics are insufficient for aggregation in solution. As a result, with these dyes the emulsion can be sensitized in correspondence with the absorption characteristics of the dye as an aggregate. Summarizing, sensitizing dyes absorb light and sensitize an emulsion bathochromically to their absorption spectrum in solution. Certain dyes, when adsorbed to the grain, absorb and sensitize to a pronounced extent in even longer wavelength regions (second order dyes) as a result of their absorption of light as aggregates.

Emulsion conditions play an important part in determining the nature and extent of adsorption of the dye to the silver halide lattice. The types of adsorption include: (1) A weakly adsorbed, probably monomolecular form. Of course, a dye which is strongly adsorbed as an aggregate when present in larger concentrations may also be strongly adsorbed even when present in amounts too small to form a complete monolayer. Strangely enough, the efficiency of transfer of the energy absorbed by the monomer is greatest, (2) A firmly adsorbed, nonwandering, probably dimeric or somewhat polymeric aggregate and, (3) A highly adsorbed, firmly bound, polymeric form.[11]

Further, some dyes even when present in minute amounts in the emulsion, absorb as aggregates. Others, form aggregations only as the concentration of the dye reaches a critical minimum. Thus, as the concentration of these latter dyes in the emulsion is increased, absorption characteristics corresponding to monomeric and polymeric forms are observed. There is also observed an intermediate form of aggregate whose absorption spectrum on the crystal is hypsochromically displaced to its spectrum in solution (H-band).

Correlation Between Photoconductivity and Sensitization

It can be stated that there is extensive correspondence between the efficiency of photoconductive response and that of photographic activity in a dye sensitized emulsion. Further, it is in just the same regions of sensitization of the emulsion by the dye (bathochromically to the absorption of the pure dye in solution) that the emulsion is sensitized for photoconduction.[12,13] One finds that those sensitizing dyes, which are adsorbed well and function as efficient photographic optical sensitizers will also extend to the longer wave-length regions the photoconductive sensitivity of a silver halide emulsion. Also, the order of photoconductive sensitizations of these dyes correspond very nearly to their order of photographic effects.

This information lends considerable weight to the proposition that sensitizing dyes function in a manner as to increase the probability of the promotion of an electron into the state of mobility required for step one of the photographic process to ensue. Since the activity of the dye corresponds to its absorption characteristics, there does not appear to be any reason to suppose that sensitization would involve the process of stopping electron mobility (step 2) or the combination of the electron with a silver ion (step 3). These latter steps of

the photographic process should not be influenced by any absorption characteristics. However, reference can be made at this juncture to the desensitization of a silver halide emulsion by a sensitizing dye. It will be indicated later that the sensitizing dye can serve as a potential sink for the excited electrons in the conduction band of the silver halide crystal and in this manner immobilize electrons. Such trapping, the precise mechanism of which will be suggested below, can convert a sensitizing dye into a desensitizer for silver halide.

It is of further interest that the phenomenon of supersensitization is observed in the photoconductivity of dyed emulsions.[12] The supersensitizer enhances the photoconductivity response to an extent over and above any enhancement of intensity of absorption of the sensitizing dye either in solution or adsorbed on the silver halide grain.[12] It is in enabling an increased efficiency in the transfer of the energy captured by the sensitizing dye (in its initial absorption) to a form useful for photoconductivity and for photographic processes that the effect of a supersensitizer is to be understood. These will be discussed separately.

From the evidence, then, the sensitizing dye absorbs the impinging radiation and this energy finally appears as an electron in the conduction band. No reference is being made as yet to the origin of the electron.

The behavior of desensitizing dyes with reference to the photoconductivity phenomenon has been treated by West.[13] It will be mentioned presently along with other characteristics of desensitizing dyes.

Mechanism of Transfer of Energy by Absorbing Dye

It is appropriate now to consider the exact path by which the energy, first acquired by the dye, is so transferred as to achieve an increased efficiency in the photographic process. As was suggested above, the sensitizing dye appears to increase the number of electrons appearing in the conduction band. It was first proposed by Mott that the absorption of light by the dye raised an electron of the dye into a conduction band. This electron was now mobile and was available for partaking in the second and third steps of the photographic process. If a dye were to absorb at a wavelength of 6500 A the energy would be of the value of 1.89 e.v. An unsensitized crystal of silver bromide is observed to promote an electron into an excited (mobile) state when it absorbs radiation of the order of 3 e.v. This could account then for the sensitization process. One need merely assume that when the dye absorbs it acquires enough energy to elevate one of its own electrons into a conduction band. Once an electron is found in an excited state, that is, in the conduction band, it is immaterial to the silver halide crystal how it originated. This excited electron can be utilized in the formation of a photographic image. If, as was expressed by Mott in this earlier picture, the origin of the electron is from the sensitizing dye itself (i.e., to an inner photoelectric effect in the sensitizing dye), it would require that for regeneration to occur an electron must be returned to the dye. Since dye molecules can sensitize with the formation of some 10 to 20 silver atoms,[14] regeneration of the dye (i.e., return of the electron) must be accounted for also. Actually, in the photographic emulsion, there is no need, nor in fact does each dye sensitize the formation of that many atoms of silver. But since the dye can do so, it can be assumed that the dye operates in the emulsion along the same path as when each dye sensitizes for one or several excitations. Now, since a practical sensitizer of the cyanine type is a cation and since loss of an electron by the dye would convert it to an even stronger (doubly charged) positive atmosphere, it would not be unreasonable to expect that the dye could capture an electron from some readily available source. Such a source for electrons would be provided by the bromide ions in the surface layers of the silver halide crystal. So the process is completed.

However, in a later article reviewing these considerations, Mott pointed out that calculations of Professor C. A. Coulson indicate that the ionization potentials of sensitizing dyes are of the order of 7 e.v.[15] This means that it takes considerably more energy for a dye than for silver halide to promote an electron into a conduction band. It becomes probable then that the sensitizing dye is not the source of the electron in that state of mobility as found in the conduction band. It must mean that the sensitizing dye somehow transfers its absorption energy to the bromide ion found on the surface of the crystal. It is the bromide ion, which takes this energy passed on by the dye, that promotes one of its electrons into the conduction band; thereby, enhancing the photographic process as a consequence of the fact that longer wavelength light becomes photographically useful.

In the original hypothesis of Mott, speculation would indicate that it was most unlikely that an electron would leave the positive Coulombic field of the cationic dye molecule. Of great interest in this connection is a study by A. Vartanian[16] of the photoconductivity characteristics of dyes. These dyes, some of which were cyanines, were precipitated on electrodes and their photoconductivity responses measured in vacuo when irradiated with wavelengths of light corresponding to their absorption spectrum. Although some dyes corresponding to the cyanine type gave a positive photoconductive response when wavelengths of light of their absorption spectrum were used, it should not be concluded that the source of the electron in the conduction band is the dye. Preferably, it can be reasoned that the dye transferred its absorbed energy to the anion associated with it, just as is believed to occur in the photographic reaction. This transferred energy then enabled the associated anion (e.g., chloride or bromide) to raise an electron into a conduction level.

In revising his original view, Mott pointed out that because of faults or other special conditions of the native silver halide crystal there is a feeble red light response of an order of 10^{-6} of its sensitivity to blue light.[15] Electrons exist in the crystal, therefore, at levels not far below the conduction band of silver halide. If the energy absorbed by the dye can be so coupled to these electrons as to effect an energy transfer, the electrons may move up into the conduction band. Further, the dyes would most likely be preferentially adsorbed and bound to the crystal surface at just those spots where faults or sensitivity centers exist. With dye polymers, Dickinson has pointed out that means are provided for

light absorbed at some more remote point to be delivered to the sensitive centers of the crystal.[17]

The exact transfer of the energy is best understood in terms of the ideas of Peierls,[18] Frenkel[19] and Franck and Teller[20] on energy propagation in crystals. In effect, when high excitation energies of light are absorbed by a crystal, an electron passes into an unfilled upper band or conduction band leaving behind a positive hole. When smaller quanta are absorbed, the electron does not escape from the field of the positive hole. Rather, the electron takes up energy to levels comparable to those assumed by an electron around an atomic core of a free atom. An exciton, or this kind of association of electron and positive hole, can be shown to be mobile. The exciton corresponds to ions or molecules, after absorption of light, in varying states of excitation up to ionization. The exciton mobility is translated as an ability to hand on the excitation energy to the various units in the crystal structure. This electronic excitation energy is propagated so swiftly through the molecules of a crystal that the retention of the energy by a particular molecule is very short in comparison with the period of excitation vibration. As a result, it can be understood on the basis of probability that the energy obtained by the dye in absorption is preferentially transferred (as an exciton migration) instead of dissipated within the molecule itself by degradation to atomic vibrations of low energy (which occurs as a slower and, therefore, less probable phenomenon). Exciton energy, though, is poorly transferred from the aggregate to the crystal. Methods of aiding this transfer are discussed under supersensitization. Of course, there will be transfer only if there is an acceptor, such as a bromide ion seated in an imperfection of the silver halide crystal with an electron at a suitable energy level available. Franck and Livingstone[21] distinguish between rapid exciton migration and slower processes. One of these slower processes, sensitized fluorescence, will be mentioned later in aiming at an explanation of certain aspects of desensitization.

Desensitization by Sensitizers and Desensitizers

Desensitizing dyes generally do not inhibit the photoconductivity of the silver halide crystal when it is irradiated by wave-lengths of light it absorbs.[13] Oddly enough, certain optical sensitizers, when converted to desensitizers by the introduction of nitro groups or the replacement of a carbon atom by a nitrogen atom in the methine chain connecting the two heterocyclic nuclei of a cyanine dye, act as sensitizers for the photoconductivity effect. Unpublished data show that certain cyanine dyes, converted to desensitizers by the introduction of a nitro group, also have small but definite sensitization for the photographic effect.[22] The photoconductivity response of the emulsion to light in the longer wavelength regions corresponds to the absorption spectrum of these dyes on the grain.[13] Most desensitizers, though, do not optically sensitize the emulsion for photoconductivity. Since no deficiency of mobile electrons can be detected in the conduction band of a silver halide emulsion irradiated with blue light when a desensitizer is present, it must follow that the desensitization effect must be associated with a later step of the photographic process. This step is apparently correlated with the ability of the desensitizer to capture the mobile electron and to function as a source of additional electron traps to those others found in the crystal. Naturally, the desensitizer trapping power is shallow compared to the applied potential used in the photoconductivity experiment, while it is deep compared to say a kink site or fault in the grain. Upon capture of the electron the desensitizer converts the electron's energy to a state no longer useful photographically. If a process utilized in degrading excitation energy is in close contiguity with the remainder of the molecule of a sensitizing dye, then there is observed a poor transfer of the absorbed energy of the sensitizer to the crystal. What is observed in terms of photoconductivity is a low sensitization by this type of dye in the region of its absorption spectrum when on a crystal. These dyes are the nitro-cyanine dyes or the azacyanines (carbon atom replaced in the chain by nitrogen atom) just mentioned above. These nitro-cyanines and azacyanines do not reduce the photoconductivity when the emulsion is exposed to blue light.[13] A nitro group is capable of vibrations of low energy which destroys the absorption structure of a molecule to which it is attached. In nearly all known cases the nitro group eliminates fluorescence.[23] Nitro groups and other electron accepting or easily reducible groups provide processes by which excited electronic energy is degraded and lost to the photographic system. Further unpublished data indicate that in the case of nitro-cyanines the desensitization by the nitro group does not occur by a degradation of the absorption structure of the parent cyanine dye.[22] Desensitization most likely is a function of the reduction potential of the nitro group.

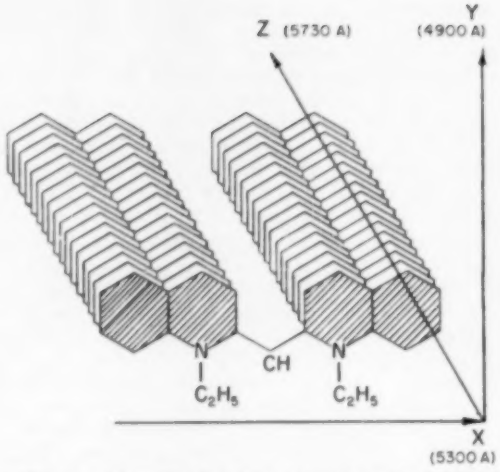

Fig. 6. Diagram showing absorption of polarized light by the pseudocyanine polymer. Characteristic absorptions are shown as the electric vector of the light is changed to the X, Y, or Z direction.

It was observed that the non-planar dyes are poorly adsorbed to the crystal. Further, the energy absorbed is rendered photographically useless probably because torsional vibrations of the non-planar dyes may preferentially degrade the excitation energy in lieu of transfer.

When geometric isomers of several styryl desensitizers were studied where greater distortion out of planarity is

10TH OPEN EXHIBIT OF TECHNICAL PHOTOGRAPHY

1954 PSA International Exhibition of Photography

Photographs are now being accepted for the 1954 Technical Division Exhibit of the Photographic Society of America to be held October 5 to 9 in the Hotel Drake, Chicago, Illinois. This exhibit reflects the latest developments of applied technical photography in all scientific and industrial fields.

William C. Crain
Chairman, Exhibition Committee

Technical Division
Photographic Society of America

"Who will see the exhibit?"

The photographs in the Technical Exhibit are viewed not only by leading photographers at the P.S.A. International Exhibition of Photography, but are displayed again and again at various public exhibitions throughout the U.S. and occasionally abroad. One way this is done is through the Technical Division's Travelling Exhibits which are selected from the exhibit each year and made available to accredited groups over a 1 to 2 year period. During this time these shows are circulated continuously to colleges and scientific institutions for one or two-week showings at no charge except shipping costs. Other prints from the Technical Exhibit are selected for the PSA Invitational Exhibitions which are displayed publicly in the larger U.S. cities, under the sponsorship of the leading photographic dealers and camera clubs in that area.

"Why should I enter photographs?"

The photographs in the Technical Exhibit will give people a keener appreciation of the true scope of investigations conducted in industrial and scientific laboratories. Your photographs will illustrate more vividly to college students and others how complex problems may sometimes be solved by photographic means, such as in high-speed photography or cosmic-ray track studies. In this way your pictures will provide a real educational service in addition to their public relations value.

"What are the entry requirements?"

The next page lists the entry procedure, and attempts to answer other questions you might have about the Exhibit. Item No. 5 is especially important as your photographs are greatly enhanced by a brief description of—"Why the picture was taken and what technique was used." The closing date for all entries is August 15, 1954. I trust we will be hearing from you soon.

CONDITIONS OF ENTRY

1. Entry is open to anyone, anywhere. Membership in the Photographic Society of America is not a requirement.

2. No entry fee is required.

3. Any type of subject matter may be chosen which utilizes industrial or scientific photography. Purely pictorial photographs of equipment or mechanical operations however will not be accepted. Practical applications of photography to technical problems are desired as well as photographs that in themselves reveal new scientific knowledge of general interest. Photographs in such varied fields as armament, agriculture, astronomy, geology, medicine and physics are welcomed. However, photographs in the fields of zoology and botany except photomicrographs should generally be entered in the P.S.A. Nature Division Exhibit.

4. Both black-and-white and color prints, and transparencies $2^1/_4 \times 3^1/_4$ inches or larger by any photographic process are acceptable.

5. Each print or series of prints should be mounted on one or more 16 × 20-inch cards if possible, or on 20 × 24-inch cards if necessary. The entries should include an outline description of the method used to make each photograph and comments explaining the purpose of the picture and its significance. This will help those viewing the exhibit to appreciate the usefulness of the photographs. We suggest that the explanatory paragraph be placed either in the lower left corner of the mount or on a separate card suitable for hanging with the entry.

6. The contributor's name and address should appear on the back of each mount. The maker's name should appear on the face of the mount.

7. There is no limit on the number of prints or transparencies that may be submitted by a contributor.

8. While all possible care will be taken to safeguard prints and transparencies, neither the Society nor the Exhibition Committee can assume any responsibility for loss or damage.

9. For your convenience and the protection of your photographs we have included an address form which may be pasted on the package containing your entries. Please use this form to mail your photographs to the George Eastman House, 900 East Ave, Rochester, New York.

10. All contributors are requested to complete the accompanying entry form and mail it to Exhibits Director, Donald B. Grim, 31 Eglantine Road, Rochester, New York.

11. Acceptance for the Exhibit will be determined by a panel of three judges. All contributors will be notified of acceptances or rejections immediately after the judging. Further selection of photographs for the Technical Division's Travelling Exhibits or PSA Invitational Exhibition will be made after the convention with notification given at that time. All photographs not included in one of these additional exhibits will be returned after the close of the convention.

12. Each contributor will receive an illustrated catalog of the 1954 PSA International Exhibition.

ENTRY FORM

P. S. A. TECHNICAL EXHIBIT 1954

All contributors are requested to complete this form and send it by 1st Class mail to Exhibits Director, Donald B. Grim, 31 Eglantine Road, Rochester, New York. Please do NOT enclose this form with your prints or transparencies.

Date_____

Exhibitor's
Name_____ Occupation_____
Last First Initial

Street Address_____

City_____ Zone____ State_____

Company Affiliation_____

Please check (√) appropriate columns or boxes TITLE OF PHOTOGRAPH	Print	Transparency	Permission is granted to retain this photograph up to 2 years if selected for the Technical Division Travelling Exhibits or P.S.A. Invitational Exhibition			
1			Yes		No	
2			Yes		No	
3			Yes		No	
4			Yes		No	
5			Yes		No	

Permission is also granted to reproduce prints and/or transparencies for publicity purposes in connection with the exhibits.

Remarks_____

Signature_____

Cut here Cut here

Personal Record —Retain this part for your files

Tenth Open Exhibit of
Technical Photography
1954 PSA
International Exhibition
Chicago, Illinois.

Title of Photograph	This entry was selected for: Technical Exhibit	Technical Division Travelling Exhibit	PSA Invitational Exhibition
1			
2			
3			
4			
5			

For Mailing All Photographs cut here

From_____

To:
PSA Technical Division Exhibit
George Eastman House
900 East Avenue
Rochester, New York

CONTENTS: Photographs for exhibition only. Do not bend. To be returned to sender. May be opened for postal inspection.

Tenth Open Exhibit
of Technical Photography
PSA Technical Division
2005 Walnut Street
Philadelphia 3, Pennsylvania

TENTH OPEN EXHIBIT OF TECHNICAL PHOTOGRAPHY

1954 PSA INTERNATIONAL EXHIBITION OF PHOTOGRAPHY

Closing Date—August 15, 1954

TENTH OPEN EXHIBIT OF TECHNICAL PHOTOGRAPHY

Judges: Walter Clark, FPSA
Arthur Neumer
Beaumont Newhall, APSA

PSA Technical Division Exhibition Committee

William C. Crain.....Chairman
Donald B. Grim.....Exhibits Director
Donald Soper.....Committee
William F. Swann, APSA.....Committee

Section Representatives

P. M. Mikoda.....Binghamton
H. Howell.....Boston
J. Jackson.....Cleveland
C. Smith.....Ithaca
H. Croix.....New York
D. Grim.....Rochester

indicated for the cis isomer over the trans, there was found a greater desensitizing power of the cis over the trans form.[24]

Now, once an electron is mobile, even the presence of a desensitizer does not diminish photoconductivity. The traps provided by the desensitizer are only efficient when compared to the traps of the silver halide crystal. It is under normal photographic conditions that the desensitizer is observed to trap the mobile electrons more readily than the crystal. When the electron is trapped by a desensitizer, it is removed from any further participation in the photographic process. However, it is conceivable that very efficient traps can be constructed in a silver halide crystal, which immobilize electrons but which do not remove them thereby from photographic usefulness. Further, if this trapping is sufficiently strong, a desensitizer for the photoconductivity effect and a sensitizer for the photographic process would appear. Indeed, that is precisely the behavior of the known chemical sensitizers such as allylthiourea.[12] So as not to oversimplify the function of chemical sensitizers, it should be indicated that they act in a dual role; they can combine with positive holes or with bromine atoms and permit the formation of a latent image through the immobilization of electrons at sensitivity spots, and they can provide nuclei for the condensation of silver atoms.[26]

A most puzzling aspect of desensitization is that produced by sensitizing dyes themselves. This effect is over and above any that can be attributed to mechanical interference or filter action by the adsorbed dye layer, although the desensitization by the dye is observed to increase with increasing concentration.[25] One might summarize the conclusions of Spence and Carroll by saying that the practical or optimum concentration for a sensitizing dye in an emulsion is determined by a balance of absorption, on the one hand, and desensitization by the dye, on the other.[25] Upon increase of concentration of the sensitizing dye, absorption and desensitization increase by different functions. When the ratio of absorption to desensitization passes through a maximum, then maximum sensitization is achieved. Moreover, Spence and Carroll also showed that there was no connection between the optimum sensitization and the saturation of the grain surface by dye.

It is felt that an understanding of desensitization by sensitizing dyes can be had by reference to concepts on sensitized fluoresence.[21] Already mentioned is the transfer of energy by an excited electron due to electronic migration and to exciton migration. Exciton migration appears to best explain the transfer of energy from the dye to the grain. The characteristic bathochromic shift when the dye is adsorbed on the grain and to even longer wavelengths when the dye absorbs on the grain as a polymer indicates strong coupling of the participants; strong coupling being a requirement for exciton migration. We have indicated that the dye transfers its energy most probably as an exciton migration since its spectrum does not indicate that sufficient energy is absorbed to raise one of its own electrons into a conduction band for energy to be transferred as an electron migration. A third means for transfer of energy can occur where there is insufficient energy for electron migration and there is inadequate coupling for exciton migration. This third type of transfer is termed sensitized fluorescence and can occur over distances of 50 A or more.[21] This type of energy transfer was first observed in a monatomic gas such as with mercury vapor. Here, absorption of 2537 A, which excites mercury, can be transferred to another metal vapor in the system. What is observed is that the resonance fluorescence of mercury is quenched and the fluorescence of the added metal vapor appears (sensitized fluorescence). Efficient transfer is obtained when the added metal can be excited to energy levels lower than the excitation level of mercury. Studies indicate that the most efficient transfer is observed when the fluorescence spectrum for the primarily excited species overlaps the absorption spectrum of the accepting molecule. Now, this process is in contradistinction to that where the primarily excited molecule emits, followed by absorption of the emitted light by a second type of molecule. A sensitizing dye and a silver halide crystal represent an ideal case of the type of transfer of energy just discussed. Farnell, Burton, and Hallama have shown[27] that the silver halides exhibit fluorescence emission spectra when measured at the temperatures of liquid nitrogen or hydrogen. These fluorescence emission spectra all lie in the visible range just to the long wavelength side of the absorption bands of the respective halides. Excitation of the fluorescence was shown to be effected by any wavelength which the halide is capable of absorbing. In the particular case of silver bromide, a weak emission in the red at 5700–6450 A was discerned and at 20 K a strong band in the green with a maximum at 5050 A. When some silver iodide was present with the silver bromide, a strong green emission band extending from 5150 A to 6000 A with a peak at 5500 A (ascribed to the iodide ion) was observed. These facts indicate that the usual sensitizing dye ranges of absorption are extremely likely to overlap the fluorescence spectrum of the silver halide. The energy of an electron in a silver halide conduction band is the same whether it is elevated by high frequency radiation (blue light) or it is in a state of high potential by virtue of its position at a crystal imperfection and acquired the extra energy to get into the conduction band by exciton transfer from the dye. Once the electron is in a conduction band, then, presumably, one need only consider the fluorescence spectrum of silver halide and the absorption spectrum of a dye acceptor to see if efficient transfer can occur. This ideal condition could serve to facilitate the transfer of the energy of the excited silver halide crystal to the sensitizing dye present in the system. It must be clearly indicated that the fluorescence spectrum (in this case that of the silver halide grain) only determines what is the ideal absorption characteristic for an acceptor (in this case that of the dye) to take up energy from the excited grain (i.e., desensitization by the sensitizing dye). It does not at all mean that silver halide emulsions must fluoresce under the usual photographic circumstances in order for this transfer of energy from crystal to dye to take place. Such a transfer can take place over an area of 50 A or more as indicated by Franck and Livingstone.[21] This would mean that desensitization manifested by a sensitizing dye is the reverse of its sensitization. The sensitizing dye accepts energy from the bromide electron at the height of the potential to which the electron was elevated, no matter how that electron was elevated. It is

in the manner in which the sensitizing dye handles this energy upon which its desensitizing powers depend. If the sensitizing dye can efficiently transfer this energy back again to the silver halide (i.e. to other bromide ions at imperfection sites of the crystal, whose electrons are not far below their conduction band), then the sensitizing dye is an efficient one. The energy removed by the sensitizing dye is reversibly put back in a manner which is photographically useful, albeit losses occur at each transfer. On the other hand, those dyes which do not transfer the energy they acquire by absorption would not be expected to return to the silver halide crystal energy they acquired in any other manner. Such dyes render energy, absorbed by irradiation with wavelengths of light corresponding to their spectrum or acquired by functioning as acceptors for the excited electrons of the crystal, into a degraded form not usable in the photographic process. Such dyes should sensitize poorly and desensitize well. One such "sensitizing dye," 3,3′-diethyl-4,4′-diphenylthiazolo-carbocyanine iodide, is known to be as potent a desensitizer as Pinakryptol green.[25]

Experiments are in progress in these laboratories to evaluate some of the above suggestions.

Supersensitization and Antisensitization

It is perhaps in the study of supersensitization and antisensitization that one finds the most straightforward evidence for believing that the sensitizing dye transfers energy and not electrons.

Supersensitization is a phenomenon of importance practically and theoretically in photography. A supersensitizer, when added in suitable amounts, enhances the sensitization of the emulsion. Many things function as supersensitizers. They can be other sensitizing dyes or compounds which themselves absorb poorly in the visible region. They appear to function only if adsorbed to the grain. The mechanism involved can best be understood by indicating successively what happens as an emulsion is dyed and then supersensitized. When a dye is combined with silver halide grains, as in an emulsion, the absorption spectrum of the original dye is shifted to the longer wavelengths and it is the dye-silver halide complex which should be considered as the absorbing constituent. Upon the addition of the dye an increased photoconductive and photographic response of the emulsion is recorded. The same emulsion with supersensitizer shows little measurable increase in adsorption of dye to grain,[28] and only slight changes in light absorption characteristics.

Now, as to changes in photographic response upon addition of supersensitizer, one must know in which form the dye appears on the grain. Is it monomeric, polymeric, or in some intermediate state of aggregation? In the case of dyes which even in incipient concentrations aggregate on the crystal or dyes in concentrations sufficient to form an aggregate (if the dye can sensitize as a polymer at all) one finds supersensitization most successfully applied. Those dyes which persist in sensitizing in a monomeric state regardless of concentration are least subject to the action of a supersensitizer. Parenthetically, it should be indicated that adsorption measurements show no difference in the type of packing of those dyes which sensitize through their polymer band and those that do not. The efficiency of sensitization (of energy transfer) is greatest for the monomer. To recapitulate: the emulsion containing dye and supersensitizer manifests no great change in adsorption or absorption characteristics over the same emulsion with dye and without supersensitizer. But the supersensitized emulsion does exhibit an increased photographic and photoconductive response. The fact that there is no great change in the absorption characteristics of the emulsion with supersensitizer should mean that there is essentially no different kind or quantity of energy being acquired. But, in view of the higher photographic and photoconductive effect, the kind and quantity of energy acquired is being more efficiently transferred. Particularly does this affect the dye polymer, which behaves as an exciton scatterer exhibiting a strong narrow absorption band accompanied by resonance fluorescence.[18,29] The supersensitizers are believed to infiltrate the dye polymer, creating faults, so that the excitation wave can pour through and more readily couple its energy over to the silver halide crystal. The dye polymer exhibits resonance fluorescence which is unique for a complicated molecule. Such resonance fluorescence means that energy primarily absorbed is being lost in a photographically useless form. Anything which would increase the efficiency by which the irradiated dye polymer can transmit the energy to a useful center would necessarily quench this fluorescence emission by the dye polymer. Supersensitizers do just that and act as fluorescence quenchers. Another known means of perturbing the dye polymer (supersensitizing) is to create faults in the lattice upon which the polymer is adsorbed. This can be achieved for example by the addition of silver iodide to the emulsion.[17] Photographically it is seen that where the non-supersensitized emulsion contains the dye as a polymer, supersensitization enhances sensitivity conferred by the dye polymer. The photographic characteristics for non-supersensitized and supersensitized emulsions differ in this case only in intensity. Where the non-supersensitized emulsion contains a dye capable of polymerization, but in too low a concentration to have many aggregates and to sensitize in any quantity through its polymer band, then the characteristics of this same emulsion, when supersensitized and non-supersensitized, differs photographically in intensity and in form. The supersensitizer increases the efficiency of energy transfer of the dye polymer, and although in this last emulsion only a few dye aggregates appear, they are rendered extraordinarily efficient. So the supersensitized emulsion in this last case has a higher photographic response in particularly the much longer wavelength regions over this same emulsion, non-supersensitized.

It is entirely conceivable that in certain cases an added substance will be adsorbed to the silver halide grain, suitably dispersed in the dye polymer, which will perturb the exciton migration but will also function in a manner as to degrade the energy involved. In this case one should selectively see a desensitization of those photographic characteristics due to the polymer band (J-band) absorption of the dye. One should also see a decrease in photoconductivity upon irradiation with the polymer band wavelength and no decrease in blue light photo-conductivity. One should detect no change in the absorp-

tion characteristics of the dyed emulsion at any wavelength. Such a substance should, like a supersensitizer, act noticeably upon dyes known to aggregate and should quench fluorescence. Such substances, essentially with the characteristics described, have been studied by West and Carroll and called antisensitizers.[28]

One difference between supersensitizers and antisensitizers deserves amplification. As stated, the action of both is best related to the transfer of energy from dye polymer to crystal. An antisensitizer helps convert the excitation induced in the polymer into a photographically useless form. Known antisensitizers themselves absorb bathochromically with respect to the dyes to which they are added. So it is not unreasonable to view antisensitization as a transfer of absorption energy from dye polymer to antisensitizer. The antisensitizer successfully competes with the crystal for the energy absorbed by the dye aggregate, captures it and then removes this energy from photographic use.[28,29] Not infrequently, however, efficient supersensitizers absorb in the ultraviolet regions while the dye whose optical sensitization they enhance absorbs green or red light. In such a case there can be no excitation to an upper absorption level of the supersensitizer by energy transfer from dye. West and Carroll have investigated the possibility of a favorable transfer from the excited singlet state of the sensitizer to the first excited triplet state of supersensitizer. They found no direct evidence for such a resonance transfer.[30] It is indicated then that in cases such as these the supersensitizer functions in a physical manner by creating distortions in the dye polymer. For some supersensitizers, alternatively, we find their absorption spectrum on silver halide suppressed when they are put to use with dye. Manifestly, this favors the view that a specialized excitation unit is formed when a sensitizer-supersensitizer combination is used. Various mechanisms for supersensitization appear to be operative.

Summary

1. A good sensitizing dye is adsorbed well to the silver halide grain; beyond that there is no correlation between adsorption and sensitization. The sensitizing dye may exist on the grain as a polymer, monomer, or in some intermediate form.

2. A good sensitizing dye is a good sensitizer for the photoconductive effect

3. Sensitization is interpreted as a transfer of energy to be utilized by the grain. Supersensitization is interpreted as providing for efficient transfer of energy from the dye absorbing as a polymer, whereas, antisensitization is taken to mean degradation of the energy absorbed by such a dye aggregation.

4. Desensitizing dyes function as traps for electrons, and are not involved in the first step of the formation of the latent image. The desensitizing action of a sensitizing dye is related to the ability of the dye to accept energy from an excited silver halide electron. If the sensitizing dye functions reversibly, it returns the energy and is a good sensitizer. If the sensitizing dye functions irreversibly and degrades the accepted energy, it is an efficient desensitizer.

Acknowledgment

Particular appreciation is expressed to Dr. Joseph S. Friedman and Dr. Lee C. Hensley of Ansco Research Laboratories for many valuable discussions and criticisms.

References

1. W. West, B. H. Carroll, and D. H. Whitcomb, *J. Phys. Chem.*, Vol. 56, p. 1054 (1952).
2. S. E. Sheppard and H. Crouch, *ibidem*, Vol. 32, p. 751 (1928).
3. S. E. Sheppard, R. H. Lambert, and R. L. Keenan, *ibidem*, Vol. 36, p. 174 (1932).
4. S. E. Sheppard, R. H. Lambert, R. D. Walker, *J. Chem. Phys.*, Vol. 7, p. 265 (1938).
5. F. London, *J. Phys. Chem.*, Vol. 46, p. 305 (1942).
6. D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, Vol. 73, p. 5691 (1951).
7. G. Scheibe, *Angewandte Chem.*, Vol. 52, p. 631 (1939).
8. S. E. Sheppard, *Science*, Vol. 93, p. 42, Jan. 10, (1941).
9. (a) G. Scheibe, *Angewandte Chem.*, Vol. 49, p. 563 (1936).
   (b) G. Scheibe, *ibidem*, Vol. 50, p. 51 (1937).
   (c) G. Scheibe, *Naturwiss.*, Vol. 25, p. 474 (1937).
   (d) G. Scheibe, *Kolloid-Zeit.*, Vol. 82, p. 1 (1938).
10. (a) E. E. Jelley, *Nature*, Vol. 138, p. 1009 (1936).
    (b) E. E. Jelley, *ibidem*, Vol. 139, p. 631 (1937).
11. H. O. Dickinson, *Phot. J.*, Vol. 88B, p. 97 (1948).
12. W. West and B. H. Carroll, *J. Chem. Phys.*, Vol. 15, p. 529 (1947).
13. W. West "Fundamental Mechanism of Photographic Sensitivity," Butterworths Scientific Publication, London, 1951, p. 99.
14. W. Lescynski, *Z. wiss. Phot.*, Vol. 24, p. 261 (1926).
15. N. F. Mott, *Phot. J.*, Vol. 88B, p. 119 (1948).
16. A. Vartanian, *Acta Physicochimica, U.S.S.R.*, Vol. 22 (2), p. 201 (1947).
17. H. O. Dickinson, *Phot. J.*, Vol. 90B, p. 142 (1950).
18. R. Peierls, *Ann. der Physik*, Vol. 13, p. 905 (1932).
19. J. Frenkel, *Phys. Rev.*, Vol. 37, p. 1276 (1931).
20. J. Franck and E. Teller, *J. Chem. Phys.*, Vol. 6, p. 861 (1938).
21. J. Franck and R. Livingstone, *Rev. Modern Phys.*, Vol. 21, p. 505 (1949).
22. L. C. Hensley, Ansco Research Laboratory unpublished report.
23. G. N. Lewis and M. Calvin, *Chem. Rev.*, Vol. 25, p. 273 (1939).
24. Work to be published by the author.
25. J. Spence and B. H. Carroll, *J. Phys. Chem.*, Vol. 52, p. 1090 (1948).
26. J. W. Mitchell, *J. Phot. Sci.*, Vol. 1, p. 110 (1953).
27. G. C. Farnell, P. C. Burton, and R. Hallama, *Phil. Mag.* (7), Vol. 41, p. 157 (1950).
28. W. West and B. H. Carroll, *J. Chem. Phys.*, Vol. 19, p. 417 (1951).
29. B. H. Carroll and W. West, "Fundamental Mechanisms of Photographic Sensitivity," Butterworths Sci. Pub., Ltd., London 1951, p. 162.
30. W. West and B. H. Carroll, *J. Phys. Chem.*, Vol. 57, p. 797 (1953).

SILVER BROMIDE PHOTO CELLS

John Eggert and Hans Amsler*

As part of an investigation of the primary photographic process under widely varying conditions, an attempt was made to follow the photolysis of binder-free silver bromide by electrical means, while the halide was enclosed between two silver electrodes one of which was light-transmitting. The resulting silver bromide photocell was prepared in the following manner: A small silver plate of about 20mm diameter was etched superficially with hot nitric acid and then brominated electrolytically (current density 30 mA/cm², for 120 sec.). After the AgBr surface was lightly polished with filter paper, a partially transparent silver coating was condensed from vapor onto the AgBr layer. Usually the transmittance of this silver layer to blue light was approximately 4%; however, it ranged in some cases as high as 15% and as low as 0.1%. The thickness of the silver bromide layer was approximately 10 microns, that of the evaporated silver layer normally 0.06 microns.

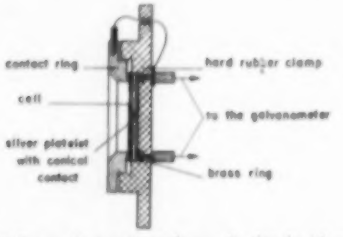

Fig. 1. Schematic section through the holder for the silver bromide cells.

Two light sources, a Phillips SP2000 high pressure mercury lamp and a 500-w projection lamp, were used to irradiate the cells in order to test their efficiency. The individual lines of the mercury spectrum were isolated by use of suitable combinations of Schott glasses, while narrow wavelength bands at corresponding wavelengths were obtained using interference filters in conjunction with the tungsten projection lamp. During irradiation, the cells furnish a photoelectric current. In the *steady state* the anterior transparent electrode provides the positive pole of the cell. Figure 1 shows in what manner the photo currents are taken from the cell; the currents are measured by a photoelectrical amplification system (galvanometer relay of Hilger, London) whose operation is shown in Figure 2. Complete details of the experimental technique as well as special experimental data appeared in 1953[1] in the thesis of H. Amsler, Federal Institute of Technology, Zurich. The present report covers briefly only the following results:

The internal resistance R_i of the cells themselves can be of very different magnitudes with different specimens of the same preparation. It is best determined by letting the cell operate at constant irradiation via different external resistances (galvanometer resistance R_g + additional resistances R_e and calculating the unknown R_i from the observed values for the photo current and the known data for R_g and R_e. Table I shows the values for R_i thus determined in the second column. Afterwards from the transmittance T of the transparent electrode (column 4) and from the magnitude of the "short-circuit current" $i_s = \frac{i_R}{T}$ ($R_g = R_e = O$) the short-circuit voltage U of the cell can be determined. Its values are shown in the 6th column of Table I. A closer investigation revealed:

1. The photo currents are strictly proportional to the radiation intensity.
2. The internal cell resistance R_i is independent of the radiation intensity.
3. The short circuit voltage U is proportional to the cell resistance in accordance with $U = 7.6 \times 10^{-4} \times R_i$; the numerical factor corresponds to the average photo current for a certain radiation intensity (based on transparency T = 1).

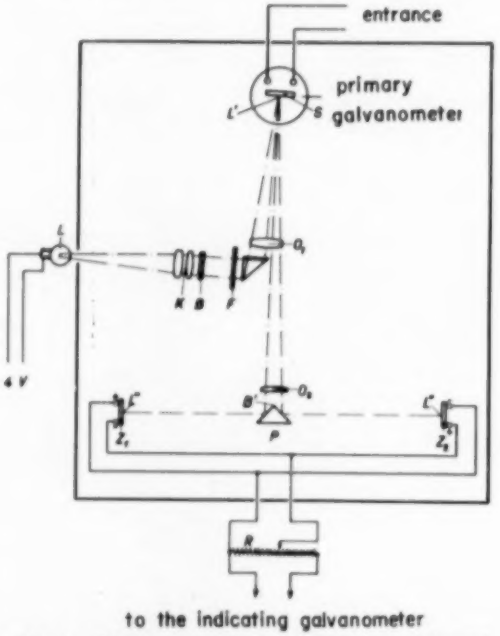

Fig. 2. Diagram showing the operation of the galvanometer relay. S = mirror of the primary galvanometer, L = light source, L′ and L″ the optical images, K = condenser, B = aperture, B′ = its optical image, O_1 and O_2 = lenses, P = ray dividing prism, Z_1 and Z_2 = barrier layer cells.

* Federal Institute of Technology, Zurich, Switzerland. Translated from the original German by G. A. Wiesehahn. Received 22 February 1954. Professor Eggert presented the subject in person at the Department of the Army, Signal Corps, Squier Signal Laboratory, Fort Monmouth, N. J. in August 1953 and again in Rochester, New York on 10 September at a special meeting of the local section of the PSA Technical Division.

Table I

CHARACTERISTICS OF DIFFERENT PHOTO CELLS

Cell Number	51	71	52	69	60	73	78	62	79
Cell Resistance R_i	61600	2350	1500	906	67	1,70	1,55	0,59	0,53
Short circuit current i_k for a constant intensity of irradiation of the cell surface	$1,81.10^{-7}$	$2,43.10^{-6}$	$8,72.10^{-6}$	$4,38.10^{-6}$	$3,33.10^{-6}$	$1,35.10^{-6}$	$1,33.10^{-6}$	$2,10.10^{-6}$	$1,48.10^{-6}$
Transparency T of the vaporized silver coating	$4,0.10^{-4}$	$1,3.10^{-1}$	$4,0.10^{-4}$	$1,4.10^{-1}$	$4,3.10^{-2}$	$1,0.10^{-2}$	$3,0.10^{-2}$	$4,4.10^{-2}$	$3,0.10^{-2}$
$\frac{i_k}{T}$ short circuit current for constant intensity of irradiation of the silver bromide layer	$4,52.10^{-4}$	$1,87.10^{-5}$	$2,18.10^{-4}$	$3,13.10^{-5}$	$7,75.10^{-5}$	$1,35.10^{-4}$	$4,43.10^{-5}$	$4,78.10^{-5}$	$4,93.10^{-5}$
$U = \frac{i_k}{T} R_i$	$2,78.10^{1}$	$4,40.10^{-2}$	$3,27.10^{-1}$	$2,84.10^{-2}$	$5,19.10^{-3}$	$2,33.10^{-4}$	$6,87.10^{-5}$	$2,82.10^{-5}$	$2,61.10^{-5}$
log U	1,444	−1,356	−0,486	−1,546	−2,285	−3,638	−4,163	−4,550	−4,584
log R_i	4,790	3,371	3,176	2,957	1,826	0,230	0,190	−0,229	−0,276

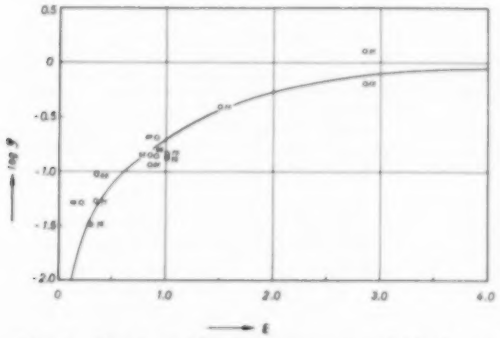

Fig. 3. The logarithm of the quantum yield of some silver bromide cells for radiation of the wavelength 365 mμ plotted against the extinction ε of the vaporized silver layer.

Operation of the Photo Cell

In order to investigate the relationship between the magnitude of the (short-circuit) photo current i_e, measured in amperes, or in electrons N_e per second, and the incident radiation E, measured as number N_q of incident quanta with a calibrated thermopile in watts/cm², the *light yield* L of the cells was determined:

$$L = \frac{i_e}{E} = \frac{N_e}{N_q}$$

If the absorption of the silver bromide for the radiation used can be determined, we can also measure besides the light yield L the *quantum yield* φ by forming the quotient from the number N_e of the electrons transported per second (calculable from i_e) and the number of the absorbed quanta (from E and the AgBr absorption A):

$$\varphi = \frac{N_e}{N_q . A}$$

In only one respect was the light yield dependent on the conditions of the preparation of the cells: While neither the current density during the bromination of the base plate nor the thickness of the generated silver bromide layer had any effect on the light yield L, i.e. on the "sensitivity" of the cell, this factor L as well as φ (determined for $\lambda = 365$ mμ) increased with the thickness of the evaporated silver layer, that is, with its decreasing transparency, as Figure 3 shows. In order to explain this strange phenomenon, one needs only to consider the formation and nature of the border surfaces between the silver bromide layer and the adjoining silver layers. If the top stratum is thin and transparent (T near 1), the processes in the cell cannot proceed in the sense of full light utilization, as it occurs when by application of a thicker silver coating the "border surface contact" is

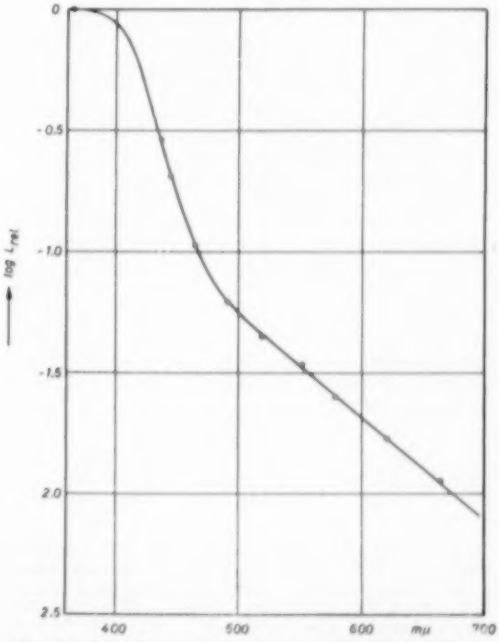

Fig. 4. The characteristic curve of the light yield (on logarithmic scale) for an unsensitized silver bromide cell plotted against wavelength.

made, so to speak, as intimate as possible. In any case it is apparent from Figure 3 that under favorable conditions factor φ very closely approaches the value 1.

Whereas the quantum yield of the cells could be determined for light of wavelength $\lambda = 365$ mμ, for longer wavelengths the light yield only could be determined, as Figure 4 shows. A very significant characteristic of the light yield (or sensitivity) curve of the cell is its break at approximately 490 mμ. It recalls very similar conditions in photographic layers. Earlier investigations[2] have shown that this break always occurs when the silver bromide of the layer has received, during the chemical ripening, additional traces of metallic silver or of silver sulfide. Curve 5 on Figure 5 shows the behavior of such a photographic layer, whereas curve 4 is that of a binder-free photographic layer which has not been ripened and consequently does not show the break. While curve 1 again refers to a cell of the usual construction and actually shows the break approximately in the same location where it occurs also in the photographic layer, curves 2 and 3 belong to a special cell. In these latter two cases, a silver plate was brominated in the usual manner, but was not given an evaporated electrode afterwards; instead, a glass plate was covered with silver by evaporation and immersed (in the dark room) for a short time in well agitated bromine water so that the mirror was covered with a thin coating of silver

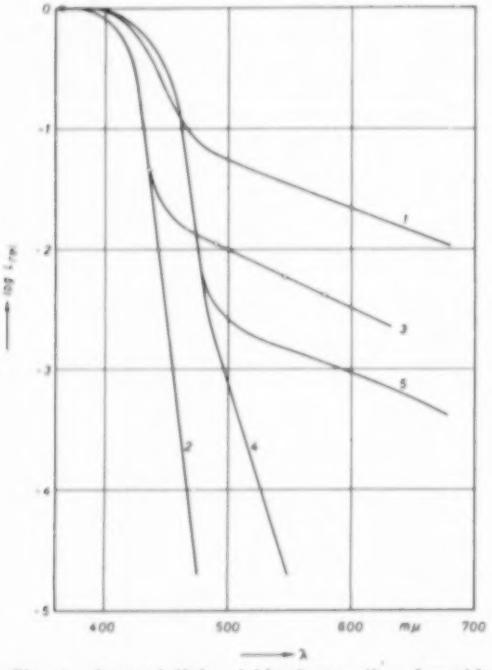

Fig. 5. Spectral light yield of two silver bromide photocells and two photographic layers on a logarithmic scale. Curve 1 refers to a cell of the customary structure (taken from Fig. 4) and the curves 2 and 3 represent a cell composed of two half elements. Curve 4 represents the course of the spectral sensitivity of a binder-free layer and curve 5 of a ripened layer containing a binding agent. The curves have been drawn arbitrarily to coincide for the wavelength 365 mμ.

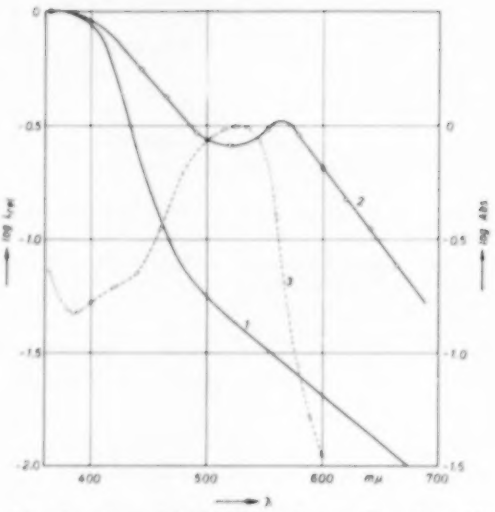

Fig. 6. Spectral light yield of two silver bromide cells on a logarithmic scale. Curve 1 refers to an unsensitized cell and curve 2 to a cell sensitized with erythrosin. The curves are arranged arbitrarily to meet at the point of shortest wavelength. Curve 3 = logarithm of the absorption of the aqueous 1:12,000 erythrosin solution used for the sensitization.

bromide. The glass plate prepared in this manner was finally pressed tightly against the brominated silver plate. The composite cell was examined as follows: On irradiation with light of the wavelengths 578 and 546 mμ the cell at first does not yield any noticeable photo current; only for $\lambda = 436$ mμ there is a strong photo current; for $\lambda = 365$ mμ the light yield increases once more and remains constant for continued irradiation, corresponding to curve 2 of Figure 5. On repeated irradiation with $\lambda = 436$ mμ, the previously measured value reappears. However, now the wavelengths 546 and 578 produce a photo current, as curve 3 of Figure 5 shows. From this experiment, it follows that the quantities of silver formed during the irradiation with short-wave light have "ripened" the cell and made it sensitive to light of longer wavelengths, just as this takes place in the normally prepared cells during the evaporation of the transparent silver electrode carried out under strong illumination, and during the ripening of photographic emulsions.

Similar parallels can be drawn when the silver bromide is given additions of silver iodide or when the cells are sensitized with dyes which are left to dry with the silver bromide layers from solutions prior to the application of the second electrode. Figure 6 may serve as an example.

As a final important property of the silver bromide cells, reference should be made to the dependence of the photocurrent upon time. Whereas a normal vacuum or selenium barrier layer cell responds to illumination without inertia, the AgBr photo cells show a pronounced induction period finally approaching the steady photo current upon which all data given so far were based. Figure 7 shows characteristic current vs. time curves for two cells with very different internal resistances. The

higher the resistance, the more slowly the limiting value of the photo current is reached and the more slowly the original zero value of the cell is reached after disconnection of the light source. If the cells contain an acceptor, e.g., $NaNO_2$ (Figure 8) even sensitized cells show a similar behavior—the cell at first produces for some seconds a photo current in the opposite direction, but soon (after passing through the zero value) changes its sign, tends towards a distinctly lower stationary value than is observed normally, and finally after cutoff of the illumination shows a "mirror image" behavior of the induction process: the photo current rises in the dark at first and a few seconds later returns to the zero value.

Explanation of the Phenomena

The current production of the cell can be ascribed quite generally to the fact that the exposure was carried out asymmetrically; the silver bromide as the active substance is exposed predominantly on that side of the cell which faces the transparent electrode. In the steady state, which shall be described first, this electrode is positive. This suggests that this positive polarization of the anterior electrode may be ascribed to the action

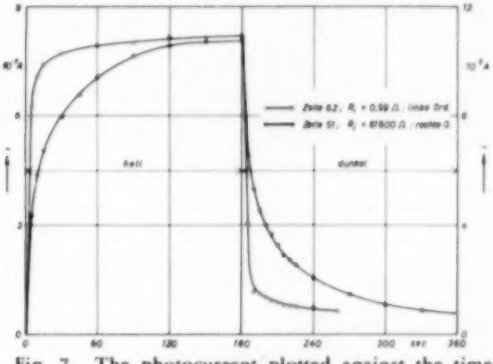

Fig. 7. The photocurrent plotted against the time after the start of the illumination and black-out (after 180 sec.) of a cell with low internal resistance (cell 62, upper curve and left ordinate) and of a cell with high internal resistance (cell 51, lower curve and right ordinate).

of the bromine formed during the photolysis of the silver bromide; for the bromine atoms (or afterwards bromine molecules) formed during the primary process according to

$$Br^- + h\nu \rightarrow Br + e^-$$

withdraw electrons from the adjoining silver electrode according to

$$Br + e^- \rightarrow Br^-$$

and confer a positive charge to the silver electrode. As a direct experimental proof of this mechanism, consider the fact that his process occurred either not at all or belatedly and to a smaller extent if the silver bromide was pretreated with sodium nitrite during the preparation of the cell. As Figure 8 has shown, the anterior electrode of the cell in this case at first assumes a negative sign, apparently because the acceptor $NaNO_2$ takes up the formed bromine more rapidly and opens the way for the

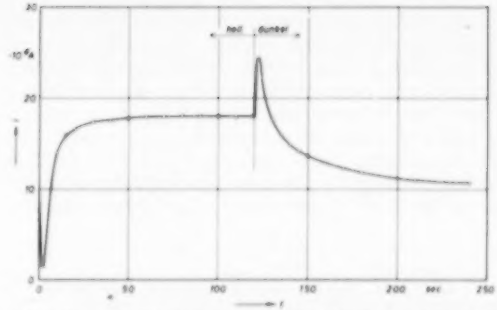

Fig. 8. The photocurrent plotted from the time after start of the illumination and black-out (120 sec) of a cell which was treated after electrolytic bromination with a 0.1 M sodium nitrite solution.

bromine to reach the silver electrode only after local impoverishment of $NaNO_2$ at least in part so that the electrode can recharge itself positively as previously without acceptor. However, because the acceptor retains its activity to a certain degree, a lower stationary value is reached than in cells free from an acceptor. Sensitizers can act similarly to sodium nitrite. In all cases in the sense of this representation—always in the steady state of cell illumination—the current production comes about because an electron current flows from the rear electrode through the outer circuit in order to compensate the positive polarization of the front electrode. If the processes occur in an extremely thin border layer next to the front electrode especially in the case of short wave light (365 mμ), and if the silver bromide and the transparent electrode are in closest contact, a condition which apparently is fulfilled especially favorably in thick evaporated silver layers (of low transparency), every bromine atom generated by the absorbed radiation can contribute to the positive charge of the front electrode so that correspondingly many electrons which are supplied by the rear electrode can be registered in the outer current circuit ($\varphi = 1$). Apparently the internal resistance R_i of the cell does not play a decisive role; rather it regulates only the voltage U of the cell according to the mentioned interrelation $U = i_s \cdot R_i$.

As far as the negative charge is concerned, which develops at the start of the illumination of a cell containing an acceptor, it must be remembered that in the photochemical primary process an electron is liberated simultaneously with the bromine atom. For this electron the transparent electrode served as an electron trap, and we are inclined to assume that the negative charge thus conferred to the front electrode would simply cancel the positive charge due to the bromine. If that were the case, the illuminated cell would not show any potential difference at all and no current production. However, normally this is not so but this state can occur only transitorily, that is, in the moment when the cell reverses its polarity during the illumination: in this exceptional state the charges reaching the front electrode just neutralize each other. If therefore the front electrode in the presence of an acceptor (or a sensitizer) cannot be reached by bromine because it is intercepted by the acceptor, there occurs a negative polarization resulting from the charging of the front electrode by the electrons

liberated during the primary process. This polarization soon again becomes positive however, because of the exhaustion of the acceptor. Nevertheless the mechanism could not occur in the described manner unless in all cases the electrons which reach the front electrode have received a special compensation. It must be assumed in addition that there occurs, as in the formation of the latent image, a simultaneous trapping of the electrons by the mobile interstitial silver ions, thus:

$$e^- + Ag^+ \rightarrow Ag$$

Their subsequent supply can be ascribed to the rear electrode which emits electrons for the outer circuit. Therefore, while in the steady state electrons flow in the outer circuit from the rear to the front electrode, within the cell silver ions travel from the rear electrode to the front. If the cell resistance R_i is small, the stationary state is reached rapidly; if R_i is large, slowly. The same holds true for the reestablishment of the rest (dark) state of the cell after cutoff of the light source. However, in this case a striking phenomenon is observed when the illumination ceases: the cell containing an acceptor showed at first a negative charge of the front electrode when the light current was turned on. In this type of cell the current production does not decrease at once when the dark pause begins, but it increases again for a few seconds, i.e. the front electrode becomes temporarily more positive. Apparently this transient state occurs because the primary electron emission which had previously opposed the flow of charge due to the diffusion of bromine, ceases with the extinction of the light. In the absence of light the slower diffusion process, which is still partially inhibited by the acceptor, causes the positive polarization of the electrode by the continued presence of accumulated bromine. That this reaction takes place even in cells free from acceptors is evident from the fact that the cell current does not become instantaneously zero upon the cutoff of the light current, but also fades only slowly.

In general this explanation of the observed phenomena appears to be in agreement with the conceptions now existing, also with those known concerning photographic layers. These experiments provided unambiguous evidence, except with regard to the mechanism of dye sensitization. It was noted that unsensitized cells on irradiation with light of long wavelengths do not yield an appreciable current and that sensitized cells do so, even with positive front electrodes. That only means that bromine atoms are formed even in the presence of sensitizers which in the sense of our conception make the front electrode positive. However, it does not necessarily mean that these bromine atoms are formed by the known exchange of electrons between the dye molecules and the Br^- lattice ions; for the same final state could be reached by an exciton mechanism.

References

1. Z. Elektrochem. Vol. 57, pp. 801–834, 1953.
2. J. Eggert, H. Arens, M. Biltz, and F. Kleinschrod, Z. wiss. Phot. Vol. 39, p. 140, 1940.

SOME NEW OPTICAL SYSTEMS FOR SPECIAL PHOTOGRAPHIC APPLICATIONS

H. Joe Meyer*

ABSTRACT

New achievements provide the opportunity to produce mirror objectives (up to 2000 mm focal length) having practical performance characteristics for functional photography. Advancement has also made available lenses of extreme wide angle (up to 142 degree angle of view). The useful application of these new lenses is discussed for the 16 and 35 mm fields.

ADVANCEMENT in optics, photographic equipment and technique is of direct and vital concern to most everyone. During periods of war there occur peaks in creative thinking, in research and development, and in production of material goods. World War II and the related defense program has affected people everywhere in one way or another. The art of photography, under this influence, has benefited greatly. The period since 1941 brought events that stimulated photography in much the same way as World War I advanced the American dye industry when great demands were made upon it. The scope of photography has been vastly expanded because of optical and mechanical achievements, as well as improved photographic technique among the photographers.

In the field of industrial and research photography, for example, the elements of time and space are brought into a more easily understood relationship, thus enabling the scientists and engineers to collect, collate and evaluate data and phenomena heretofore hidden or at least not fully understood. Photography of the visible has been taken for granted in the past. Now photography of the invisible is commonplace, extending the visible spectrum into both the ultraviolet and the infrared.

This article will discuss a few of the relatively new advances in special optical systems and techniques. Many of these advances were precipitated if not created

* Wollensak Optical Company, Rochester 21, New York.

Presented at the PSA National Convention in Los Angeles, California, 5 August 1953. Received 19 September 1953.

by the exigencies of World War II. The discussion will be mainly in terms of 16mm film sizes although, generally speaking, the lenses referred to are also suitable for 8mm, single and double 35mm cameras and even $2^1/_4 \times 2^1/_4$ inch film sizes.

Extreme Wide Angle Lenses

Where an extremely wide field of view is required the new 142° wide-angle lens, f/1.5 in speed, focal length of 3.7mm, may be useful. Another recent lens is the 84°, focal length of 5.4mm, f/1.5 in speed and with 8 elements. The systems of the lenses are basically reversed telephotos in form.

Extreme depth of field is provided in these as in all wide-angle lenses, even at the maximum aperture of f/1.5, because of the very short focal lengths. They also show small residual aberrations with the exception of distortion. The distortion, which must be expected, is characteristic of extreme wide-angle lenses of high relative aperture. In other words, these lenses provide a circular picture but still an acceptable one for problems where wide angles of view are required. Projection printing with correct optics could be worked out to correct postive prints of negatives made from these lenses. A hemispherical screen will restore the image and eliminate distortion. The Jam Handy Co. has done some work with such a system in making Aerial Gunnery Training Films. If mathematical determinations are desired, then the distortion can be corrected by proper calibration. This problem and other phases of the use of these lenses is amplified in a paper[1] by Gilkeson and Turula.

The history and development of the 142° lens are well covered in a paper by Bauer and Blake[2] of Douglas Aircraft Company describing the problems confronting them in 1948 and the research leading to development of this lens system.

Original specifications called for these wide-angle lenses on three cameras: (1) the Bell & Howell 35mm ultra-speed camera, (2) the Modified Filmo (with speeds of up to 200 pictures per second), developed jointly by Bell & Howell and Training Aids, Inc., and (3) various models of the Fastax Camera manufactured by Wollensak Optical Company. This optical system can be used for other than high-speed motion picture work, and often to the photographer's advantage where extreme wide-angle is necessary, although the resolving power is lower than that of lenses of more conventional design.

The 84° lens, not so extreme in angle, will find even greater potential usage in industrial and research fields. Consideration is being given to the use of this lens for underwater studies where wide angle and maximum apertures are required in the study of marine life. Photography in cramped quarters (such as in the cockpit of an airplane) would be facilitated by the use of this lens.

The optical system of the 142° lens comprises a Wollensak 25mm f/1.5 Cine Raptar lens as the positive component, in conjunction with a negative lens of 25mm focal length. The separation of the two components or lens systems can vary from about 6 in. to 7 in., depending on the actual angle of view desired. During manufacture this construction is customarily set for 140° angle in compliance with Douglas specifications and drawings.

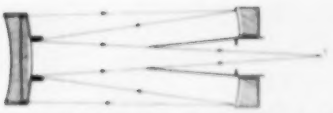

Fig. 1. Light path through a Mirrotel lens showing the "folding" effect.

The production units, which are the result of joint efforts of engineers of both companies, are available for general use.

Another lens which should be mentioned is the 12.7mm f/1.5 Cine Raptar for 16mm cameras. This lens was designed to fill the need for a distortion-corrected lens with minimum residual aberrations where extreme coverage is not a requirement. It has a diagonal coverage of 56°. This $^1/_2$ in., f/1.5 lens has had a broad acceptance because it is wide angle but not to the point of any sacrifice in quality, and it, therefore, covers a greater range of application.

Mirror Optics and Spherical Mirrors

The utilization of aspheric and spherical mirrors is not new. The spherical mirror alone has objectionable spherical aberration, even though this aberration is 8× smaller than that of a single refracting lens of equal aperture and focal length. (This is true even when the lens has the most favorable bending for minimum spherical aberration.)

Where high resolution and overall highest quality performance are essential considerations, any spherical aberration affecting these requirements is intolerable. Therefore, in the past, mirrors were parabolized by hand correction. (A highly skilled time-consuming process involving elaborate and painstaking testing methods.) In conjunction with the primary paraboloidal mirror, a hyperboloidal or ellipsoidal secondary mirror was necessary to assure spherical aberration correction while relaying the image out of the system for observation or recording on film. Hand-figuring the secondary mirror was also a tedious and highly skilled art.

The advantages of optical mirror systems are such that other ways to achieve an aberration-free system were sought and devised through the years. The Newtonian system, one of the simplest, was followed by the improved Cassegrain system, and the further improved but less desirable Gregorian system. In 1930, Schmidt corrected the spherical aberration of the spherical mirror with one aspheric corrector plate. In recent years, the ultimate goal—perfect correction with all spherical components—has been reached with the all new Mirrotel Catadioptric telephoto objectives. The 18 in. Delft lens, referred to later, and other mirror optics are described in a survey of work on optics in the Netherlands during the last war or immediately before written by Bouwers.[3] This book, "Achievement in Optics," reports on mirror optics development carried on by Bouwers and his associates, much of which was done underground during military occupation of the Netherlands.

The first successful instrument employing mirror optics that was manufactured in America is the Mirroscope, a 20 × 50 telescope or spotting scope made by Wollensak. Now there are three additional focal lengths available in photographic objectives namely: 20 in., 40 in. and 80 in

Fig. 2. The 20 inch long Mirrotel lens, having a focal length of 80 inches, mounted on a 35mm miniature film camera, or vice versa.

This uniformly graded scale of focal lengths was developed for the convenience of photographers and engineers.

Probably the most important advantage of optical mirror systems is the complete absence of chromatic aberration (no special focusing for infra-red). There is no secondary color and no lateral color to degrade the image. Because the light path is "folded" three times (Figure 1) within the system, the length and weight are less than $^1/_3$ those of an equivalent refractive system. The greater stability thus attained is extremely important for long focus objectives; ease of operation, and overall performance. Example: A conventional 80 in. refractive telephoto lens would be 68 in. long, measured from focal plane to front lens. The 80 in. Mirrotel (Figure 2) is only 20 in. from focal plane to front. This same ratio applies to the 20 in. Fototel and 40 in. Mirrotel. The Fototel was on the market in the 18 in. size, commonly known as the Delft Lens, and was previously made in the Netherlands.

The Mirrotels are concentric systems, therefore the straight line containing the center of curvature parallel to any given ray of light may be regarded as an axis of the system. There is no coma, astigmatism or distortion. This means that the high quality axial image is maintained at all extra axial image points. The mirror surfaces and all glass to air surfaces are treated with the anti-reflection hard coating, Wocote.

The physical limit of resolution is attained in the Mirrotel as defined by Lord Rayleigh on the basis of the Airy Disc.[4] To minimize associated focus shift caused by temperature variation, the very sensitive mirror surfaces and the associated air spaces are maintained by mountings employing Invar rods.

The 20 in. lens with relative aperture of f/5.6 has an angular coverage of 1.2° on 16mm film and has 3 elements. The 40 in. lens with a relative aperture of f/8 has an angular coverage of 0.58° with 3 elements and a photographic resolution of 40 lines per mm. The 80 in. lens with a relative aperture of f/14, has a coverage of 0.29° on 16mm film with 2 elements and a photographic resolution of 50 lines per mm.

Filters are housed in a turret at the rear of the lens on the 40 in. and 80 in. sizes. The 20 in. lens accepts a filter on the front barrel. The turret rotates and is indexed to locate filter position.

Standard optical glass filters are supplied, the red (A-25), yellow (K-2), orange (G), and neutral. The neutral filter is a haze filter and an optical path compensating filter which should be used when focusing.

Most of the lenses discussed can be used on the Bell & Howell Cameras including the high speed modified Filmo, the Eastman Kodak High Speed Camera and the Wollensak Fastax Camera, to name the high speed units on the market. Then in addition most normal speed intermittent cameras will accept these lenses, too. The Mirrotels can be adapted to practically all the double frame 35mm still cameras that have removable lenses. These wide-angle, high-speed refracting lens systems and mirror telephoto systems developed in recent years are typical of the progress that is being made in increasing the application of photography by industry and science. The importance of photography was well expressed by Ansel Adams when he wrote—"Photography, next to the printed word reaches, instructs, interprets, clarifies and modulates opinion more than any other medium of communication and expression."

References

1. "Optical Aids for High Speed Photography" by David C. Gilkeson and A. Eugene Turula. December 1952 Journal of the SMPTE Vol. 59.
2. "Application of Wide Angle Optics to Moderately High Speed Motion Picture Cameras" by H. E. Bauer and A. W. Blake. January 1953 Journal of the SMPTE Vol. 60.
3. "Achievements in Optics" by A. Bouwers, Elsevier Publishing Co. Inc., New York, N. Y.
4. "New Optical Mirror Lenses" by David C. Gilkeson, 1952 Vol. 3 No. 4 of "Photographic Engineering." And general extract from Wollensak brochure on Mirrotel lenses.

Fig. 3. Landscape views illustrating the magnification obtained by using an 80 inch Mirrotel Telephoto objective instead of a 2 inch lens at a distance of $3^1/_2$ miles from the farm buildings.

AN INORGANIC DEVELOPER REACTIVATED BY ELECTROLYSIS

A. A. Rasch and J. I. Crabtree, F.P.S.A.*

ABSTRACT

The inorganic developer system of Roman, employing essentially a solution prepared from vanadium pentoxide, sulfuric, and hydrobromic acids, and reduced by electrolysis has been further investigated. With positive emulsions, the speed values were appreciably greater than with conventional processing; but with negative emulsions, excessive fog values were frequently encountered. Development was very rapid, even at low temperatures, full development being obtained in from 20 to 50 seconds at 60 F, depending on the material. A continuous processing machine for motion-picture positive film was devised in which initial developer activity was continuously maintained by electrolysis, replenishment being made only to balance carry-over losses.

Solutions of certain metal ions have been known for some time to have photographic activity. Rather extensive investigations have been made of a developing system employing ferrous iron as the active agent,[1] while some work has been done on systems using chromium,[2] tungsten,[3] and molybdenum.[2] Recently, experimental data have been given[4] on systems in which metal ions and a chelating agent are used as the developing agent, particularly good results being obtained with iron and titanium ions. However, none of the systems have found much practical use because of their low activity, poor stability, and short exhaustion life.

For some time past, divalent vanadium has also been known to have photographic activity. In 1894, A. and L. Lumière described the preparation of a vanadium developer solution.[5] However, few experimental data were given and a subsequent reference[6] did not add to this information.

The recent investigations of Pierre Roman,[7] a French photographic chemist, have revived interest in the inorganic developer systems. Roman calculated that a metal-ion system having a standard reduction potential more negative than +0.120 volts would reduce silver bromide in a silver bromide–bromide ion system. He decided to limit investigation to developers that would be of some practical interest and, therefore, the systems had to meet the following requirements: (1) The system should not be greatly affected by reasonable changes in concentrations of the oxidized and reduced form of the active agent, and (2) the oxidized and reduced forms of the active agent should be soluble and dissociated.

With these requirements, Roman found that the systems listed in Table I were of possible interest. Tin was immediately eliminated because its nonselective development characteristics, and the chromium system was also found to give extremely poor fog-to-image ratio. The trivalent–tetravalent titanium system was found to be too inactive, and the divalent–trivalent titanium system too unstable. Tungsten required the use of hydrofluoric acid to keep it in solution, making its use impractical.

The vanadium solution could be readily prepared, however, and was a very active developer. Roman found that an acid solution of electrolytically reduced vanadium gave especially good results on motion picture positive-type emulsions. Since the divalent–trivalent vanadium system is reversible, an exhausted developer solution can be regenerated by electrolysis which reforms the active divalent vanadium ion. As will be seen, this method is a feature of the use of the vanadium system.

Since Roman's original work was published, an extensive investigation of the vanadium developer system has been undertaken in the Kodak Research Laboratories. Although all varieties of emulsions have been tested using the vanadium system, particular emphasis has been placed on finding the optimum formula for use with motion picture positive-type emulsions on which best results were obtained. An experimental machine has been designed for processing with a vanadium developer which includes a means of maintaining developer activity by electrolytic regeneration.

Table I

METAL ION SYSTEMS WHICH WILL REDUCE SILVER BROMIDE IN A SILVER BROMIDE–BROMIDE-ION SYSTEM

$Ti^{4+} + e = Ti^{3+}$	$E =$	0.03 to 0.06 volts	pH = 1 to 3
$W^{6+} + 3e = W^{3+}$	$E =$	0.0 to 0.06 volts	pH = 0
$V^{3+} + e = V^{2+}$	$E =$	−0.2 to 0.06 volts	pH = 0
$Ti^{3+} + e = Ti^{2+}$	$E =$	−0.4 to 0.06 volts	pH = 1
$Cr^{3+} + e = Cr^{2+}$	$E =$	−0.4 to 0.06 volts	pH = 0
$Sn^{4+} + 2e = Sn^{2+}$	$E =$	−0.7 to 0.06 volts	pH = 11

Preparation of the Developer

Only a few vanadium compounds are commercially available and, although a salt of vanadium would be most desirable as a starting compound, the cost of the salts is prohibitive. Vanadium pentoxide is by far the cheapest of the compounds but is somewhat difficult to compound in a developer, owing to its low solubility in water or dilute acid solutions.

A. Solubilizing the Vanadium Pentoxide

Roman described a method of preparation in which sulfur dioxide is bubbled through a mixture of the vanadium pentoxide and hydrobromic acid. Sulfur dioxide reduces the vanadium from the pentavalent to the readily soluble tetravalent state and the resulting solution can then be electrolyzed to form the divalent vanadium.

This method was used in the preparation of the solutions for the preliminary experiments of the current investigations. However, it was soon found that traces

* Research Laboratories, Eastman Kodak Company, Rochester 4, New York. Received 7 January 1954.

of sulfur dioxide left in solution later formed compounds that greatly increased the fogging propensity of the developer. Since it was quite difficult to remove the last trace of sulfur dioxide from solutions, alternative methods of preparation were sought.

Vanadium pentoxide will slowly dissolve in hydrobromic acid, the bromide ion reducing the pentavalent vanadium and forming bromine gas. The reaction is accelerated greatly by adding concentrated sulfuric acid to the solution and heating. This method was used for some time but was always considered objectionable because of the necessity of disposing of a considerable quantity of highly corrosive and noxious bromine gas by-product.

More recently, it was found that the vanadium pentoxide could be readily reduced and solubilized by a solution of oxalic acid in moderately concentrated sulfuric acid. Carbon dioxide gas is given off as a by-product, and, since the other reaction product of the oxalic acid is water, no ions are left from the reducing material that will later affect photographic results. This reaction is much preferred, especially when preparing large batches, since it is easy to control and eliminates the necessity of handling noxious gases. The equations illustrating the various methods of preparation are given in Table II.

Table II

REACTIONS SHOWING THE VARIOUS METHODS OF PREPARING VANADIUM DEVELOPER SYSTEMS

I. *Solubilization*

$V_2O_5 + 2HBr + SO_2 \xrightarrow{(H_2SO_4)} 2VOSO_4 + VOBr_2 + H_2O$

$V_2O_5 + 6HBr \longrightarrow 2VOBr_2 + 3H_2O + Br_2$

$V_2O_5 + H_2C_2O_4 + 2H_2SO_4 \rightarrow 2VOSO_4 + 2CO_2 + 3H_2O$

II. *Reduction*

(a) *Chemical*

$2VOSO_4 + Zn + 2H_2SO_4 \rightarrow V_2(SO_4)_3 + ZnSO_4 + 2H_2O$

$V_2(SO_4)_3 + Zn \rightarrow 2VSO_4 + ZnSO_4$

(b) *Electrolytic*

$VO^{++} + 2H^+ + e \rightarrow V^{+++} + H_2O$

$V^{+++} + e \rightarrow V^{++}$

(c) *Cell Reactions Occurring During Reduction*

$2H^+ + 2e \rightarrow H_2$

$2H_2O \rightarrow O_2 + 4H^+ + 4e$

$2Br^- \rightarrow Br_2 + 2e$

B. Production of the Photographically Active Divalent Vanadium

Once the solution containing the tetravalent vanadium has been formed, the extra acid, as required by the developer formula, is added and the solution is diluted to volume.

To prepare the photographically active divalent vanadium, the solution can be either chemically reduced or electrolyzed. The Lumières prepared their solutions by reducing with zinc metal. Although this reaction goes fairly rapidly, the use of zinc is undesirable, since impurities in the metal make it a fairly active reducer of hydrogen ion so that the total acidity of the formula is affected.

To reduce the vanadium electrolytically, a method essentially the same as that used by Roman has been employed. The solution is placed in a cell consisting of a noncorroding cylindrical tank made from materials such as Plexiglas or Type 316 stainless steel. A sheet lead liner insulated from the tank constitutes the cathode, and an unglazed porcelain cup centered in the tank contains a graphite rod, which serves as the anode.

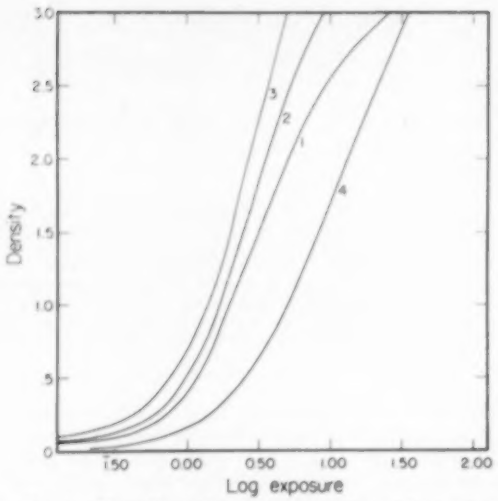

Fig. 1. Vanadium development compared to conventional development. Eastman Fine Grain Release Positive Film, Type 5302, developed 20, 28, and 40 seconds at 60 F in vanadium developer (curves 1 to 3) shows a two stop speed advantage over the same film (curve 4) developed 4½ minutes at 68 F in Kodak D-16 developer.

The vanadium solution serves as the catholyte, while the anolyte consists of a sulfuric acid solution equal in total acidity to that of the developer solution.

Direct current is supplied to the cell from a selenium rectifier or a d-c generator. Suitable provision is made to stir the solution in the cathode compartment, and the whole unit is surrounded by a cold-water cooling jacket.

A current density of 250 amperes per square meter is maintained on the cathode. The laboratory cell described draws about 30 amperes at a potential of 5 to 6 volts across the cell. The reduction process is accomplished at a current efficiency of 70 percent, with the result that this cell can prepare the usual developer solution at the rate of about 1 liter per hour.

C. Chemistry of the Electrolytic Reduction of Vanadium

The reduction process takes place in two steps. Tetravalent vanadium is first reduced to the trivalent state and, when this reaction is complete, the trivalent vanadium is reduced to the divalent state. The first step proceeds to completion using only slightly more than the theoretical current consumption, the small loss in current efficiency being due to heat evolution. However, the second step of the reaction never does go to completion and, in reducing 80 to 85 percent of the trivalent vanadium to the divalent state, current efficiencies of less than 50 percent prevail. This loss of current efficiency is due to hydrogen gas formed at the cathode as a side reaction which is in competition with the vanadium-reducing reaction.

Actually, it would be expected that this gas side reaction would be predominant, since the Standard E.M.F's

of the two systems would indicate that hydrogen ion would more readily accept an electron than the trivalent vanadium. However, owing to the fact that the lead cathode has a high overvoltage to the hydrogen gas forming reaction, the reduction of vanadium will occur more readily. The reaction is not eliminated completely, and when about 60 to 70 per cent of the vanadium has been reduced to the divalent state, hydrogen gas begins to form at the cathode and the rate of formation increases rapidly as electrolysis proceeds. It has been found impractical to carry the electrolysis beyond the point where 85 percent of the vanadium has been reduced, since current efficiency at this point is very low. From a photographic standpoint, further electrolysis is unnecessary since the developing capacity of the solution at this point is ample.

During the early stages of electrolysis, oxygen forms at the anode, but as electrolysis proceeds, a certain amount of bromide ion diffuses into the anode compartment and is immediately oxidized to bromine, but in the preparation of the developer the amount of bromide ion that diffuses into the anode compartment is not enough to affect the developer composition significantly. In the case of a long-term electrolysis, proper balancing of the concentrations can be made to offset the effect of electrolysis.

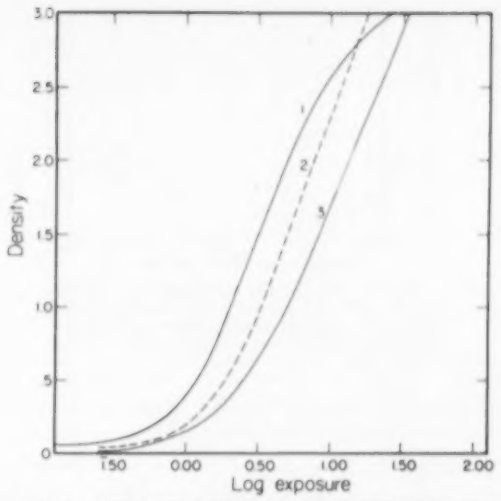

Fig. 2. Vanadium development compared to conventional and high-energy development of Eastman Fine Grain Release Positive Film, Type 5302. Curve 1: 20 seconds at 60 F in vanadium developer; Curve 2: 28 seconds at 80 F in Kodak SD-26; Curve 3: 4½ minutes at 68 F in Kodak D-16.

Properties of Vanadium Developer

A. Development of Eastman Fine Grain Release Positive Film, Type 5302

The solution prepared as already described is an extremely active developer, especially when used to process Eastman Fine Grain Release Positive Film, Type 5302. As shown in Figure 1, development for times ranging from 20 to 40 seconds at 60 F produces sensitometric properties very similar to those produced in 4½ minutes at 68 F in a conventional Metol-hydroquinone developer such as Kodak D-16. One outstanding difference in sensitometric properties produced by vanadium development is the more than two times increase in speed. Shoulder densities, however, tend to be somewhat low during the short development times and fog values will tend to be a little high unless proper precautions are taken.

Of particular interest in this case is the rapid rate of development that is obtained at lower than normal temperatures. Development to produce normal gamma with this film requires about 20 seconds at 60 F as compared to 28 seconds at 80 F in a high-energy developer such as Kodak SD-26. A comparison of the results produced by the three types of developers is shown in Figure 2.

B. Formula Variation to Produce Optimum Results

Roman obtained best results with a vanadium developer solution 0.4*M* in vanadium and 2.35*M* in hydrobromic acid. He also tried sulfuric and hydrochloric acid solutions of vanadium but obtained lower image densities and much higher fog values.

Roman's optimum experimental formula did not give best results when used with Eastman Fine Grain Release Positive Film, Type 5302, available in this country. The formula used to produce the results shown in Figure 1 was the result of experiments in which a systematic variation of the various developer components was made.

The optimum vanadium-ion concentration was found to be 0.35 to 0.45*M*, which is in agreement with Roman's work. However, better results were obtained with a mixture of hydrobromic and sulfuric acids rather than by using either one alone.

The fogging propensity varied quite widely with the sulfuric and hydrobromic acid concentrations, minimum fog values being obtained when the ratio of the equivalent sulfuric acid to hydrobromic acid concentration was 4:1. Fog and speed values varied somewhat with the total acidity of the developer having the optimum 0.44*M* vanadium concentration, a total acidity of 3.0*N* being found to be about optimum.

Combining these values, a formula 0.44 molar in vanadium, 80 to 85 percent of which is in the divalent state, 2.4 normal in sulfuric acid, and 0.6 molar in hydrobromic acid gave best results on motion picture positive-type emulsions. In terms of weight and volumes of starting materials, the optimum experimental formula was as follows:

Vanadium pentoxide	40 grams
Hydrobromic acid (48%)	68 milliliters
Sulfuric acid (95%)	68 milliliters
Water to make	* 1 liter

(28 Grams of oxalic acid were used to dissolve the vanadium pentoxide.)

Since this formula tended to give slightly higher than normal fog values on ciné positive types of emulsions, the addition of antifoggants was investigated. Conventional organic antifoggants, such as benzotriazole and 6-nitrobenzimidazole, were found to have no effect on the fogging propensity. However, low concentrations of potas-

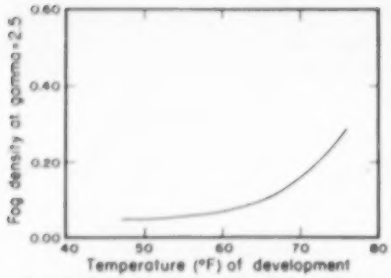

Fig. 3. Fog density produced for a given degree of development in vanadium developer at various temperatures using Eastman Fine Grain Release Positive Film, Type 5302.

sium iodide, in the order of 0.05 gram per liter, maintained fog at acceptable levels.

C. *Photographic Chemistry of Vanadium Development*

The temperature of development, while controlling development rate, has an appreciable effect on fog formation. Best results, as shown in Figure 3, are obtained at temperatures of 60 F or below. Above 60 F, fogging increases sharply for a given degree of image development. It has also been found that fogging will vary widely from sample to sample of the same type of emulsion at the higher temperatures, even though there are no differences in sensitometric results when these samples are processed in a conventional developer.

The temperature coefficient of development is low, as shown in Figure 4, being about 1.5 for a 18 F (10 C) change of temperature. As has been pointed out, the temperature coefficient of fog development is higher, with the result that the vanadium developer has less selectivity at higher temperatures.

Using a positive type of emulsion, the kinetics of vanadium development were extensively investigated by T. H. James and L. J. Fortmiller, of these Laboratories,

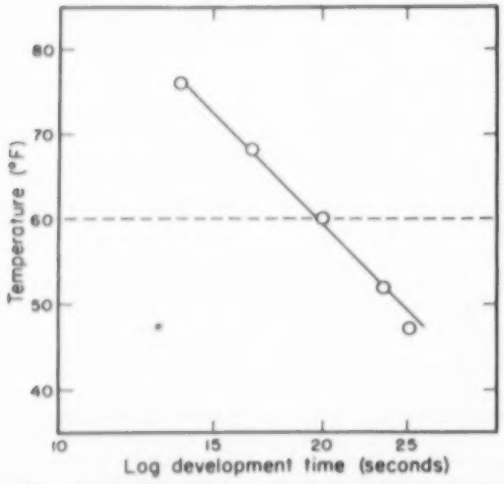

Fig. 4. Development time vs. development temperature in vanadium developer to produce gamma = 2.5 on Eastman Fine Grain Release Positive Film, Type 5302.

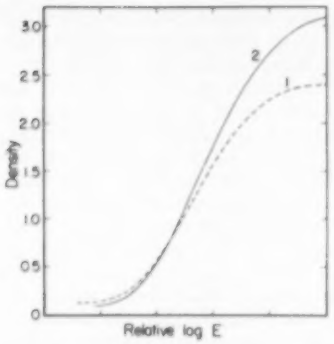

Fig. 6. Effect of degree of agitation on vanadium development. Curve 1 was produced by still development and curve 2 by using highly agitated development for the same time.

and the complete description of this work appears in a forthcoming article.[5] The development reaction can be most simply stated as follows:

$$V^{++} + Ag^{+} = Ag + V^{+++}.$$

James and Fortmiller found that the rate of development is proportional to the concentration of vanadous ion up to a concentration of 0.1*M* but it drops somewhat below direct proportionality at higher concentrations, and the rate is essentially independent of vanadic-ion concentration.

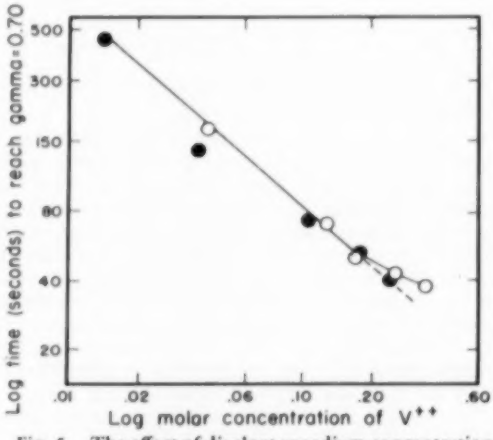

Fig. 5. The effect of divalent vanadium concentration on development rate of Kodak Super-XX Panchromatic sheet film. X-X-X = Ratio of divalent to trivalent vanadium concentrations constant. O-O-O = Divalent vanadium concentration varied, trivalent vanadium concentration = 0.44*M*.

Although James and Fortmiller's work was done with special apparatus, eliminating secondary effects such as solution exhaustion and aeration, tests by the authors using conventional processing techniques and a negative type of emulsion gave very close to the same results. Figure 5 shows that development rate was completely dependent on divalent vanadium concentration, whether or not total vanadium concentration was kept constant or varied proportionally to divalent vanadium concentration.

The rate of development under most practical conditions appears to be largely controlled by the rate of diffusion of developer through the gelatin layer, and there-

fore is markedly influenced by agitation. The differences in sensitometric properties produced by varied agitation are demonstrated by the curves in Figure 6. When comparing high agitation with still development, it is seen that for the same time of development much higher shoulder densities and higher gamma are obtained when high agitation is used.

D. Effect of Vanadium Development on Various Photographic Materials

Since best results have been obtained with fine-grain positive types of emulsions, most of the preliminary work was done with this material in order to develop a practical method for the rapid processing of 35mm motion-picture release prints. Testing of other varieties of photographic materials has been made using the optimum experimental positive film developer. Therefore, the results obtained to date do not necessarily represent the best that can be obtained with the optimum variation of the vanadium developer formula.

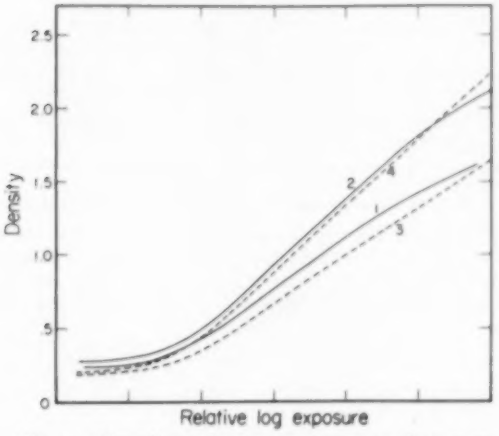

Fig. 7. Vanadium development compared to conventional development of Kodak Super-XX Panchromatic sheet film. Curves 1 & 2: 40 and 60 seconds at 60 F in vanadium developer; Curves 3 & 4; 4 and 7 minutes at 68 F in Kodak DK-50 developer.

The characteristic difference in results produced between vanadium-processed positive and negative emulsions is that large increases in speed compared with conventional development are not obtained with the negative films.

1. *Amateur and Professional Film.* Of the amateur and professional negative films tested, fairly good results were obtained on Kodak Super-XX Panchromatic sheet film developed 40 to 60 seconds at 60 F. As shown in Figure 7, fog values tend to run high and shoulder densities low when compared to conventional processing in a developer such as Kodak DK-50. At best, speed values obtained are equal to those obtained by conventional processing but will generally tend to run low, especially if an attempt is made to control fogging.

When developing other negative sheet and roll films in the vanadium developers, much poorer results were obtained. The major difficulty involved was the high

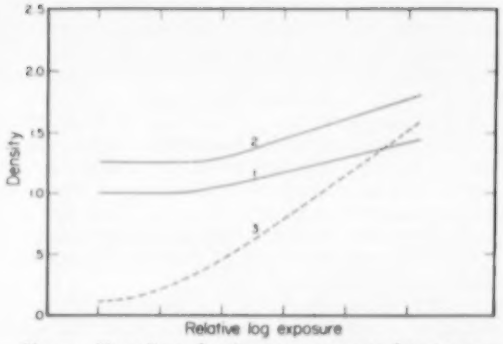

Fig. 8. Vanadium development compared to conventional development of Kodak Super Panchro-Press Type B sheet film. Curves 1 and 2: 28 and 40 seconds at 60 F in vanadium developer; Curve 3: Typical curve produced by development in Kodak DK-50 developer.

fogging propensity of the vanadium developer. Extremely high fog-to-image ratio constituting almost non-selective development was obtained on Super Panchro-Press Type B sheet film (Fig. 8) and Kodak Plus-X roll film. Some suspicion exists that these results are not a developer characteristic or a characteristic of one particular type of emulsion. There appears to be a variation of fog developed on different samples of the same emulsion, an effect similar to that already noted in the case of positive-type emulsions developed at high temperatures. On other occasions, much poorer results than those shown have been obtained with samples of Super-XX Panchromatic sheet film, while better results have been obtained on the Super Panchro-Press film.

2. *Professional Motion Picture Film.* The same has been found to be true when processing motion picture negative emulsions. Fairly good results such as those shown in Figure 9 can be obtained on Eastman Plus-X Panchromatic Cine Negative film while poor results such as obtained on Eastman Super-XX Panchromatic Cine Negative (Fig. 10) are also obtained.

The potassium iodide antifoggant has no significant effect on reducing fog of the high-fogging emulsions.

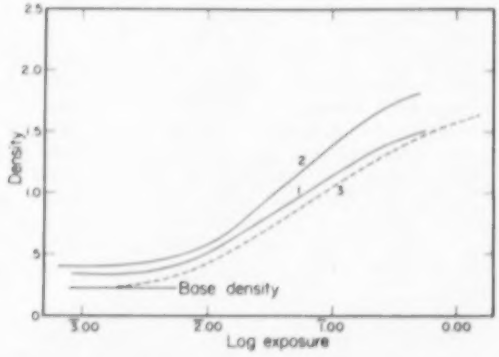

Fig. 9. Vanadium development compared to conventional development of Eastman Plus-X Panchromatic Cine Negative Film. Curves 1 & 2: 28 and 40 seconds at 60 F in vanadium developer; Curve 3: 6½ minutes in Kodak SD-28 developer.

An attempt was also made to obtain better results by using a more dilute developer for longer development times, but to no avail. In all cases, there was no indication of inferior results with any of the emulsion samples when developed by conventional means.

It is not possible at the present time to establish definitely the development characteristics of the negative emulsions in the vanadium developer system until further study has been made of the factors that affect sensitometric properties. At best, it can be said that vanadium development produces results on high-speed negative emulsions somewhat poorer than those produced by conventional development.

3. *X-Ray Film.* In the case of x-ray emulsions, more encouraging results have been obtained on the samples investigated thus far. As shown in Figure 11, results produced by vanadium development of Kodak Industrial X-Ray Film, Type M, in 25 seconds at 60 F compare very favorably with 5 minutes' development in the Kodak Rapid X-Ray Developer. Speed has been increased somewhat although fog values tend to run higher. Similar results were obtained on Kodak Blue-Brand Medical X-Ray Film.

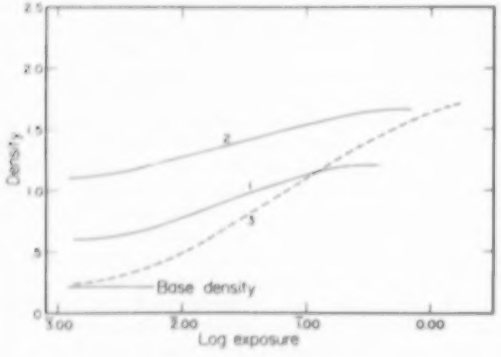

Fig. 10. Vanadium development compared to conventional development of Eastman Super-XX Panchromatic Cine Negative. Curves 1 & 2: 28 and 40 seconds at 60 F in vanadium developer; Curve 3: 9 minutes at 68 F in Kodak SD-28 developer.

4. *Recording Film.* In the field of fine-grain recording emulsions, exceptionally good results have been obtained on Kodak Microfile Film. As shown in Figure 12, the large increases in speed over conventional processing, associated with fine-grain positive types of emulsions, are also evident in this case. Twenty seconds at 60 F in the vanadium developer produces approximately twice the speed obtained in 6 minutes at 68 F in Kodak D-11 Developer. At the same time, resolving-power and graininess tests made on vanadium-developed samples have indicated that they are at least unchanged if not slightly improved, over those produced by conventional processing.

5. *Printing Paper.* When processing paper emulsions, development by vanadium is very rapid and characteristics noted with the processing of fine-grain positive emulsions are also evident. As shown in Figure 13, 5 seconds' development of Kodak Velox F Printing Paper, Grade 2, gives similar sensitometric properties to 60 seconds' development at 68 F in Kodak Dektol Developer,

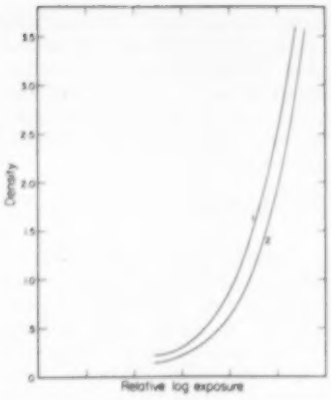

Fig. 11. Vanadium development compared to conventional development of Kodak Industrial X-ray Film, Type M. 80-KV X-Ray exposure using ultraspeed screen. Curve 1: 25 seconds at 68 F in vanadium developer; Curve 2: 5 minutes at 68 F in Kodak Rapid X-Ray Developer.

diluted 1:2. Here some difficulty is experienced in controlling development because of the very short times necessary to reach normal gamma. Fog values increase rapidly when longer development times are used.

The results discussed so far represent a rough survey of the effect of vanadium development on photographic materials and are by no means absolute nor do they represent the best possible results that can be obtained in each case. Until systematic formula variations can be nade in an attempt to obtain optimum results on each type of emulsion, it is not wise to make any final conclusions.

E. Physical Characteristics of Vanadium-Developed Images

The characteristics of images produced by vanadium development have been studied in the case of Eastman Fine Grain Release Postive Film, Type 5302, and have shown some marked differences from those produced by

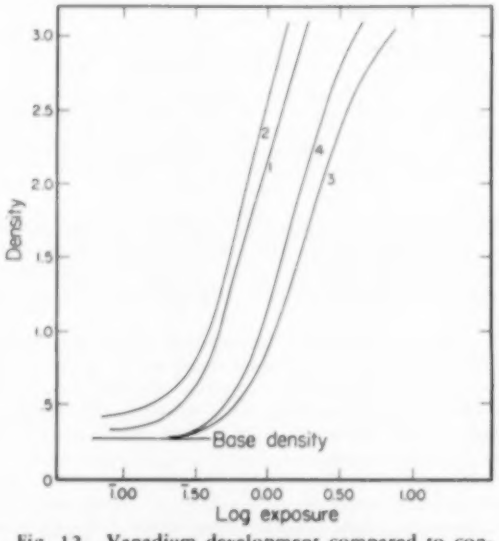

Fig. 12. Vanadium development compared to conventional development of Kodak Microfile Film. Curves 1 & 2: 20 and 30 seconds at 60 F in vanadium developer; Curves 3 & 4: 4 and 6 minutes at 68 F in Kodak D-11 developer.

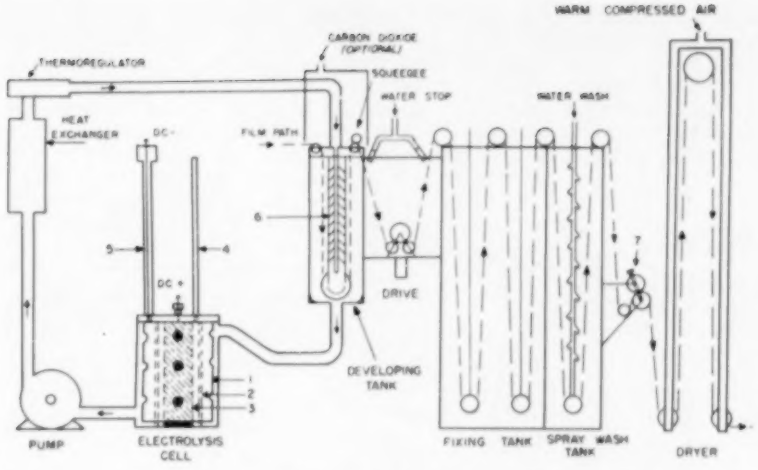

Fig. 15. Schematic representation of vanadium processing machine: 1. lead cathode; 2. porous cup; 3. carbon anode; 4. anode compartment vent; 5. cathode compartment vent; 6. column of orifices through which developer is forced to give immersed-jet agitation; 7. drive and squeegee. Arrows in developer recirculation system show the direction of solution flow. The electrolysis cell, the developing tank, and the drying cabinet are of Plexiglas, while all other parts that come in contact with solutions are of Type 316 stainless steel.

conventional developers. Photomicrographs of cross sections of a vanadium-developed image show that image silver tends to be concentrated more towards the surface of the emulsion than is the case with conventionally developed images. Where there is high fog, "fog silver" is predominantly deposited near the base, and the extent of this fog silver varies inversely with the amount of image silver produced.

The image tone produced by vanadium development on Eastman Fine Grain Release Positive Film, Type 5302, is somewhat colder than that produced by conventional development but the graininess of the two images remains essentially equal. In terms of speed-graininess ratio, vanadium development appears to give a considerable improvement over conventional processing.

The relatively high acid concentration of the vanadium developer is necessary to prevent hydrolysis of the vanadous ion and subsequent precipitation. The high acidity will cause serious swelling or dissolving of the gelatin unless the photographic emulsion used is prepared with hardened gelatin, or is hardened before development.

The physical stability of fine-grain positive emulsions when processed in vanadium solutions is excellent, despite the extreme acidity of the solution. This is due, in part, to the short development time, the low temperature of processing, and the hardening power of the vanadium ion. If temperature of processing is raised to 75 F, softening and reticulation of the emulsion may occur, even during short developing times.

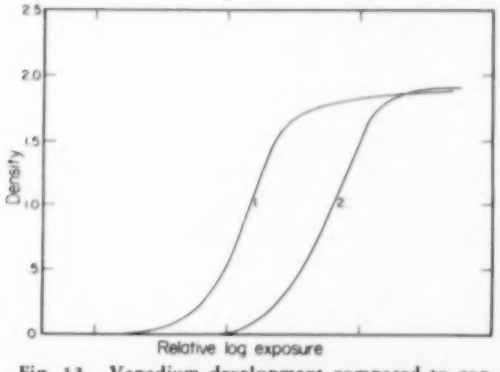

Fig. 13. Vanadium development compared to conventional development of Kodak Velox Printing Paper, Grade 2. Curve 1: 5 seconds at 60 F in vanadium developer; Curve 2: 60 seconds at 68 F in Kodak Dektol developer diluted 1:2.

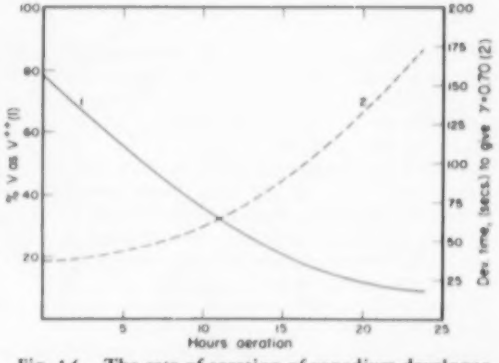

Fig. 14. The rate of aeration of vanadium developer. Curve 1: Hours of aeration vs. divalent vanadium concentration of developer. Curve 2: Time required to develop Kodak Super-XX sheet film to gamma = 0.70 in aerated developer vs. hours of aeration. Data are for 1 liter of developer standing in 1½-liter beaker at room atmosphere conditions.

F. Stability of Vanadium Developer

The stability of the vanadium developer in terms of resistance to aeration is very poor in comparison to most conventional film developers. As shown in Figure 14, almost complete oxidation of the developer occurred within 24 hours when a 1-liter sample of the developer about 3 inches deep having a surface area of 15 square inches was exposed to room atmosphere conditions. If the developer is agitated without provision being made to exclude air, the oxidation will occur much more rapidly. Therefore, it is necessary, despite the high capacity of the developer, to exclude air as much as is reasonably possible during processing. Developer solutions stored in full, tightly stoppered bottles, however, do not deteriorate.

The developing experiments described here were made using a 250-cc. cylinder. After the film was immersed in the solution, the cylinder was stoppered and then shaken to provide the high agitation required. By using this procedure, up to twelve 35mm filmstrips could be processed in a 250-ml. sample of developer without aeration causing losses in activity that would affect sensitometric results.

A Vanadium Processing Machine

The various experiments leading to the results already described were made using hand-processing techniques. As a step towards reducing the vanadium development system to practice, a small continuous processing machine was built for processing projection lengths of motion-picture prints. The authors are indebted to Mr. C. J. Kunz, of the Kodak Camera Works, who was instrumental in working out the design and specifications of the vanadium processing machine.

A. Design

Because of the highly corrosive nature of the vanadium developer solution, the developing section must be made from noncorroding materials, such as Plexiglas and Type 316 stainless steel. Figure 15 shows a schematic representation of the vanadium processor.

Immersed jet-agitation is used in the developing tank and the developer from the tank flows through an electrolytic cell similar to that already described. The developer is pumped from the cell through a thermostatically controlled heat-exchange system back to the immersed jets of the developing tank.

The electrolytic cell in the system serves as a novel method of maintaining developer activity. Oxidized vanadium formed by the development process and aeration is electrolytically reduced in the cell and the composition of the developer remains essentially constant. The only loss is represented by the amount of solution carried out on the film, and with proper squeegeeing, this may be kept at a low level. Runs have been made where carry-out rates of approximately 0.3 milliliter per foot of 35mm film have prevailed.

After development, the film immediately passes through a spray water rinse which acts as a stop bath. From this point, the film is conventionally fixed, washed, and dried, except that an ammonium hypo fixer, spray wash, and warm, forced-air current are employed, so that the rate of these processing steps will be consistent with the developing rate. Figures 16 and 17 show the experimental machine with which the vanadium development tests were made.

B. Processing Procedure

With the optimum experimental vanadium developer formula, Eastman Fine Grain Release Positive Film, Type 5302, is developed in 15 to 20 seconds at 60 F on the experimental machine with a film speed of about 6 feet per minute. The developing section is charged with a solution prepared in an external electrolytic cell, the electrolysis being performed external to the machine primarily to save time. Continuous electrolytic regeneration of the vanadium developer during a processing run requires relatively little current and consequently the electrolytic cell in the machine need not have a very high capacity. However, if the machine were filled with unelectrolyzed developer at the start, it would require an unreasonable amount of time to bring the solution up to proper activity with the low-capacity machine cell.

Replenishment to maintain volume of solution in the system can be made with either the electrolyzed or nonelectrolyzed solution. The replenisher solution has essentially the same composition as the starting solution, with the possible exception of a slightly lower bromide concentration. At the carry-out rates found on the machine, as much as 3,300 feet of 35mm film can be processed in 1 liter of vanadium developer solution. The bromide build-up in the developer caused by this high processing capacity will be at least partially compensated for by the electrolysis. Bromide ion diffusing into the anode compartment of the machine cell is oxidized to bromine gas and thus removed from the system. If this is not enough, the composition of the replenisher solution is adjusted accordingly.

C. Practical Tests

Runs of up to 8,000 feet have been made on the processing machine with Eastman Fine Grain Release Positive Film, Type 5302. Electrolytic regeneration of the developer was used, as already described, to maintain developer activity, and throughout the run it was possible to produce reasonably constant photographic results.

To keep a check on the developer composition during processing, an analysis procedure has been devised that requires no more equipment, time, and skill than the procedure used in control analysis currently practiced by motion-picture processing laboratories.

There appears to be no necessity for special techniques in processing other than to observe the following precaution: Since the vanadium solution is very sensitive to aerial oxidation, care must be taken to prevent undue exposure to air, otherwise very rapid oxidation of the developer will occur and there will be a tendency towards aerial fogging.

A carbon dioxide gas blanket was maintained over the developing tank head on the experimental machine since there was a tendency for air to be sucked into the system. It is believed, however, that an improvement in design will eliminate this necessity and the slight oxidation that would occur could be balanced by electrolytic regeneration.

D. Potential Applications

At present, the only immediate potential users of the vanadium system are large-scale laboratories processing motion-picture positive film that already have the necessary facilities and skilled personnel. The advantages of rapid development rate, effective speed increase, improved image tone, and high capacity of the vanadium development system are offset by the necessity of handling a corrosive solution, a noxious gas, and using special equipment. Further study and development will be necessary to determine the ultimate practicability of the vanadium system, but it represents a pioneering effort in the use of inorganic salts for developing photographic emulsions.

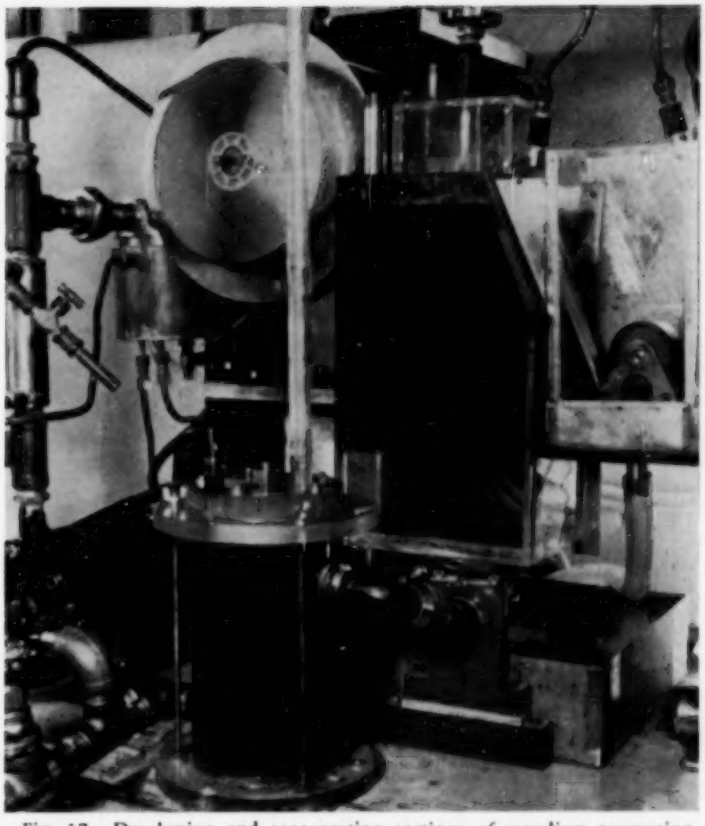

Fig. 17. Developing and regeneration sections of vanadium processing machine. The oxidized vanadium formed by the development process and by aeration is electrolytically reduced in the cell shown in the foreground.

References

1. C. E. K. Mees, "The Theory of the Photographic Process," The Macmillan Co., New York, N. Y., 1942, pp. 332–337.
2. E. Fuchs, "Entwicklung photographischer Schichten auf electrischem Wege," *Phot. Ind.*, Vol. 28, p. 927, 1930.
3. R. E. Liesegang, "Entwicklungs-Versuche," *Phot. Arch.*, p. 282, 1895.
4. (a) J. Rzymkowski, "Titan (III)-Oxolat als Photographischer Entwickler," *Arhiv Za Kemiju*, Vol. 20, pp. 26–45, 1948.
   (b) See also J. Rzymkowski, "Metallkomplexsyteme des Typus $Alk_x\ (R\text{-}COO)_y\ Me_z$ als photographische Entwickler," *Z. wiss. Phot.*, Vol. 40, p. 136, 1941.
5. A. and L. Lumière, "Sur les propriétés des sels de vanadium," *Bull. soc. franç. phot.*, Vol. 10, p. 108, 1894 (2).
6. Tobin, *Druggist Circular*, Vol. 43, p. 184, October 1899.
7. P. Roman, "Préparation et régénération électrolytiques de révélateurs photographiques," *Sci. et ind. phot.* (2), Vol. 23, pp. 417–426, 1952.
8. L. J. Fortmiller, and T. H. James (to be published in *J. Phot. Sci.*) formerly Sect. B, *Phot. J.* of Roy. Phot. Soc.).

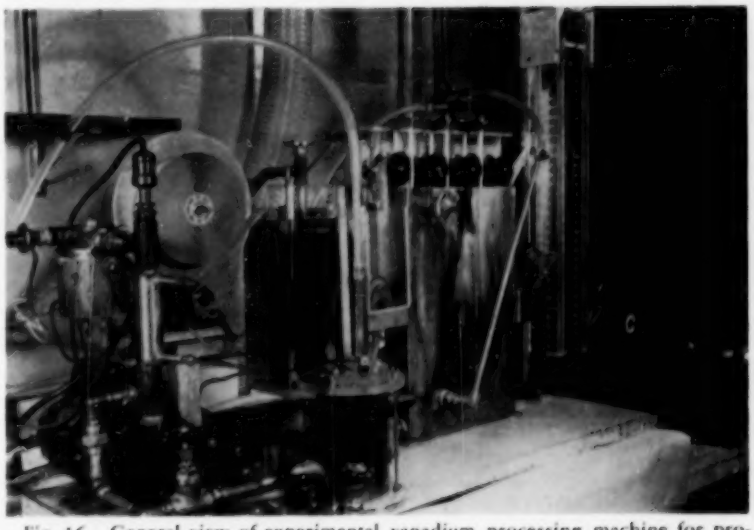

Fig. 16. General view of experimental vanadium processing machine for producing projection lengths of 35mm motion picture films. Because of the corrosive nature of the vanadium developer solution, materials such as Plexiglas and Type 316 stainless steel are used in the construction.

MICRORADIOGRAPHY AND AUTORADIOGRAPHY SYMPOSIUM*

A symposium on micro- and autoradiography was held on 17 December 1953 at the Institute of Physics, London, by the Scientific and Technical Group of the Royal Photographic Society.

The first part of the meeting was devoted to microradiography and gave evidence of the potentialities and limitations of the method. The first speaker Prof. G. A. G. Mitchell, Anatomy Dept., Manchester University explored the potential uses of microradiography of biological objects, such as body tissues, leaves, seeds, fibres, hairs, insects, wings, ova, small crustacea, etc. He described methods of enhancing contrast by using various injections and by soaking or impregnating tissues and materials with solutions which were more or less radioopaque. The speaker came to the conclusion that in most respects microradiography is less valuable than histological and histochemical methods in investigating the structure and composition of biological objects. On the other hand the following advantages of microradiography were stressed: (a) Much thicker sections can be examined and thus the arrangement of various structures can be traced over greater distances than is possible in ordinary 5–10 microns histological sections. (b) Structures containing bone or calcareous deposits can be examined without preliminary decalcification. (c) Normal or abnormal deposits of radioopaque substances are readily detectable. (d) The distribution of vessels and tubules can be studied accurately and fairly rapidly by the method. (e) It provides a means of accurate measurement.

Mr. R. V. Ely, London, dealt with the requirements of apparatus such as "sealed off" and "demountable" x-ray tubes, backing and diffusion pumps, valves, vacuum gauges, high tension and filament supply units, main voltage stabilizers, vacuum cassettes etc. A demountable x-ray tube developed by the speaker permits easy removal of the window in order to attach an extension cylinder holding a $^1/_4$-plate at a considerable distance from the target. The apparatus can be used for photographic as well as for direct magnification. In the latter case only very small focal spots are permitted.

Whereas the first two speakers chiefly dealt with magnifications up to 500 times, the third speaker Dr. V. E. Cosslett (Cavendish Laboratory, Cambridge) looked for magnifications of the order of one thousand diameters and above. He therefore prefers the term "x-ray microscopy" to "microradiography." Since the optical resolving power is limited to about 0.5 micron by the wavelength of light, a higher resolving power should be possible using x-rays of a wavelength of the order of 1 Angstrom Unit. As the contrast attainable is roughly proportional to the cube of the wavelength of the x-rays, practical considerations demand the use of wavelengths of one or several angstroms (i.e. 12 kV x-rays and below are required). Four basic methods of x-ray microscopy were suggested: (1) the conventional contact method, where object and film are in close proximity; the other methods are those of direct magnification by means of (2) bent crystals, (3) mirror reflection and (4) endwindow x-ray tubes. The relative merits of these four methods were reviewed and the end-window technique developed by the author was described in greater detail. It involves the production of an ultra-fine focus on an end-window target, using electron optical techniques. The use of very thin windows makes high x-ray intensity available from spots of the order of one micron in diameter. At present the speaker and his coworkers are attempting to obtain a focal spot of the order of 0.1 micron. High direct magnification is obtained by bringing the specimen close to the window. Several examples of Cosslett's method for examining the microstructure of biological and metallurgical specimens were shown. Photographs were taken of living insects, in order to follow up radiation damage in insects when exposed to various x-ray doses.

The second part of the meeting was entirely devoted to biological autoradiography. The techniques of micro-autoradiography are mainly based on the use of stripped Nuclear Track emulsions. At present the refinement of methods appears to be in the foreground of autoradiographic investigations and, in particular a deeper insight into the problems of resolution and quantitative uptake of radioisotopes is required. Dr. S. R. Pelc, Radio-Therapeutic Research Unit, Hammersmith Hospital, London, reviewed autoradiography by discussing the possibilities and limitations of the method. The incorporation of radioisotopes into the organism depends on the correct choice of the chemical compound of interest and the concentration, which in turn is dependent on the sensitivity of the film material to be used. In the preparation of the specimens, special care has to be taken in regard (a) to possible loss of radioactive compounds due to solvents (b) to the possibility of the formation of artefacts caused, e.g. by chemical interaction between specimen and photographic material. Several examples of the possible ambiguity and pitfalls in interpretation were given.

Dr. L. F. Lamerton (Department of Physics, Royal Cancer Hospital, London) discussed problems involving the resolution and sensitivity in autoradiography. In contrast to the theoretical treatment of resolution by Doniach and Pelc, L. F. Lamerton defines resolution as the distance (d) if the images of two uniformly active cylindrical sources of diameter (d) can just be resolved when the centres are separated by a distance (2d). A table showing the resolution, in terms of microns, obtainable for various emulsion and specimen thicknesses and for various distances between specimen and film was given.

Dr. L. G. Lajtha (Radiotherapy Department, Churchill Hospital, Oxford) described a high resolution autoradiographic stripping film technique adapted to smears made from human bone marrow cultures in vitro. Such smears where the cells are in a mono-cellular layer will spread out at a suitable distance from each other (to prevent cross-fire) and the flotation of the emulsion on 25 C distilled water for 4-6 minutes yields preparations with suitable geometry for high resolution. The autoradiographs were stained after processing to facilitate recognition of the individual cells. The method is sensitive enough to detect and localise as little as 20–30 ^{32}P or 30–50 ^{35}S atoms per cell.

Experiments were described on the mechanism of desoxyribonucleic acid (DNA) synthesis as measured with ^{32}P and adenine ^{14}C. The timing of the cell cycle and DNA synthesis and the determination of the rate of DNA synthesis allow the classification of different cell types on their growth rate. Experiments on the ^{35}S sulphate uptake have shown that uptake of inorganic ^{35}S sulphate and its incorporation into a substance related to the chondroitin sulphates is a specific function of the myeloid cells in the bone marrow.

* Contributed by the Scientific and Technical Group of the Royal Photographic Society of Great Britain.